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Toko et al.

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(54) **MAGNETORESISTIVE ELEMENT AND METHOD OF MANUFACTURING THE SAME**

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(51) **Int. Cl.**

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H01L 21/8239	(2006.01)
H01L 43/10	(2006.01)
H01L 43/12	(2006.01)
H01L 43/08	(2006.01)

(52) **U.S. Cl.**
CPC ***H01L 43/08*** (2013.01); ***H01L 43/10*** (2013.01); ***H01L 43/12*** (2013.01); *H01L 27/228* (2013.01)
USPC **257/425**; 438/3

(58) **Field of Classification Search**
CPC H01L 43/12; H01L 43/10; H01L 43/08; H01L 27/228
USPC 257/E43.004, E27.005, E21.665
See application file for complete search history.

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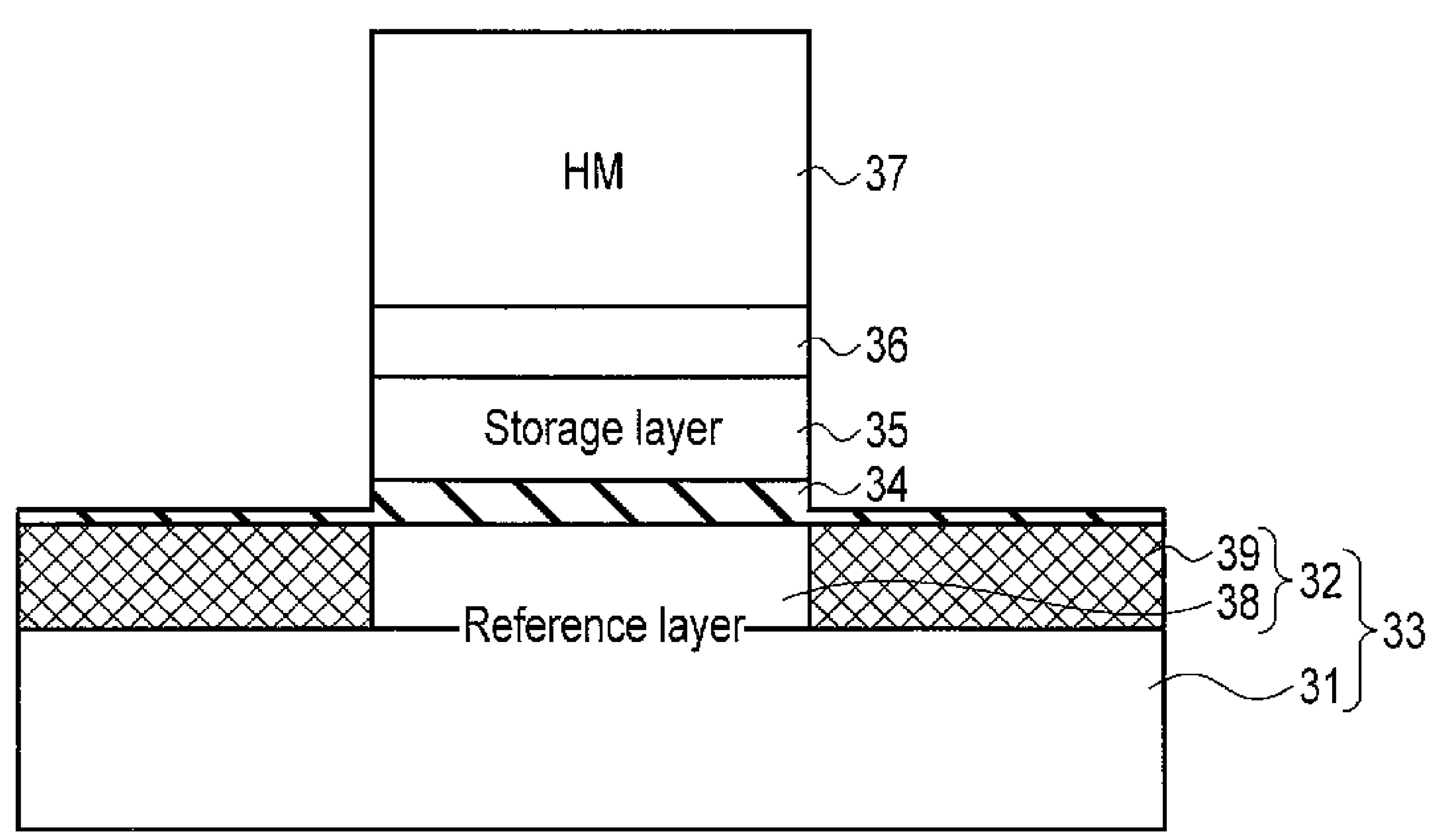
(57) **ABSTRACT**

According to one embodiment, a magnetoresistive element comprises a first magnetic layer having a magnetization direction invariable and perpendicular to a film surface, a tunnel barrier layer formed on the first magnetic layer, and a second magnetic layer formed on the tunnel barrier layer and having a magnetization direction variable and perpendicular to the film surface. The first magnetic layer includes an interface layer formed on an upper side in contact with a lower portion of the tunnel barrier layer, and a main body layer formed on a lower side and serving as an origin of perpendicular magnetic anisotropy. The interface layer includes a first area provided on an inner side and having magnetization, and a second area provided on an outer side to surround the first area and having magnetization smaller than the magnetization of the first area or no magnetization.

15 Claims, 12 Drawing Sheets



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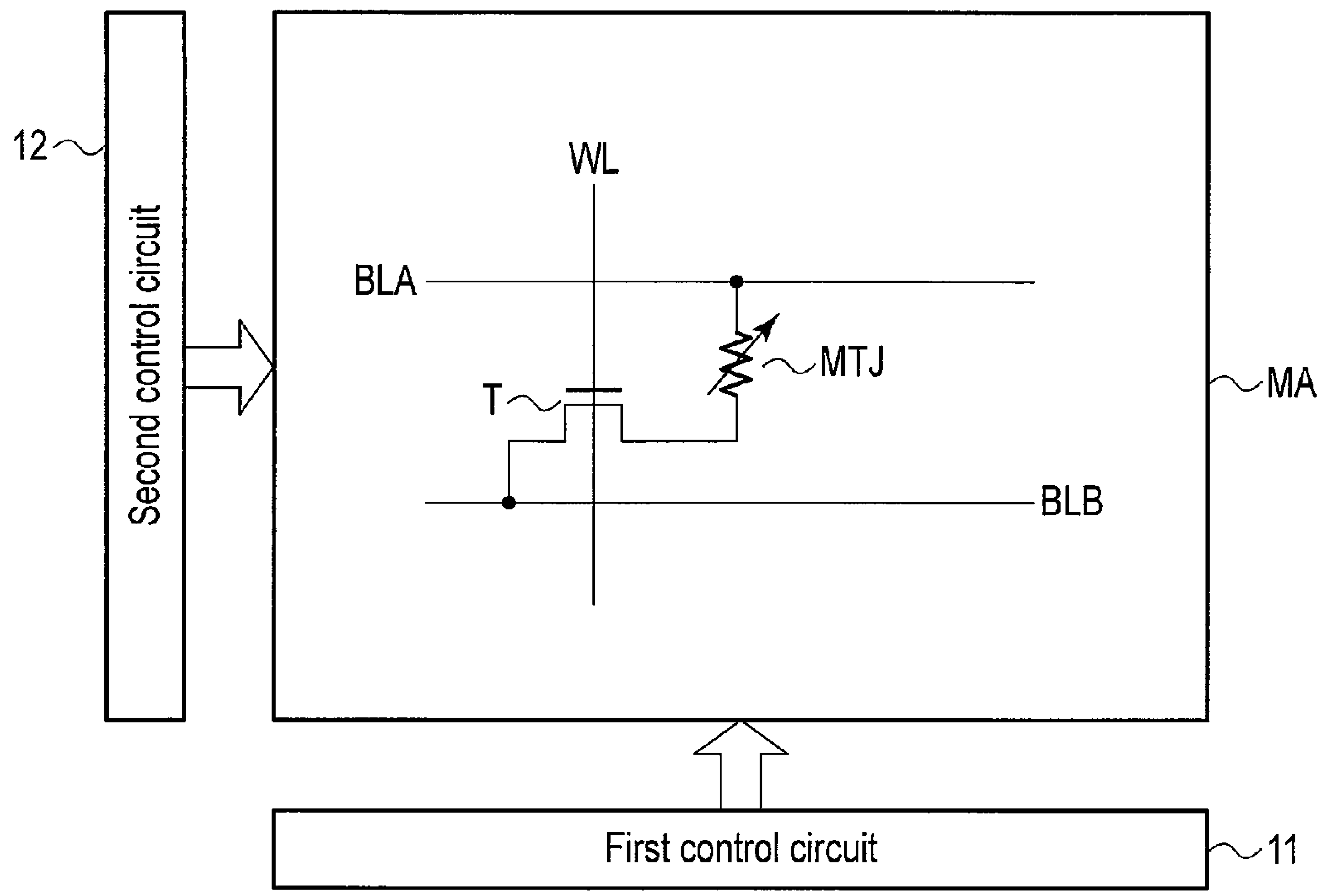
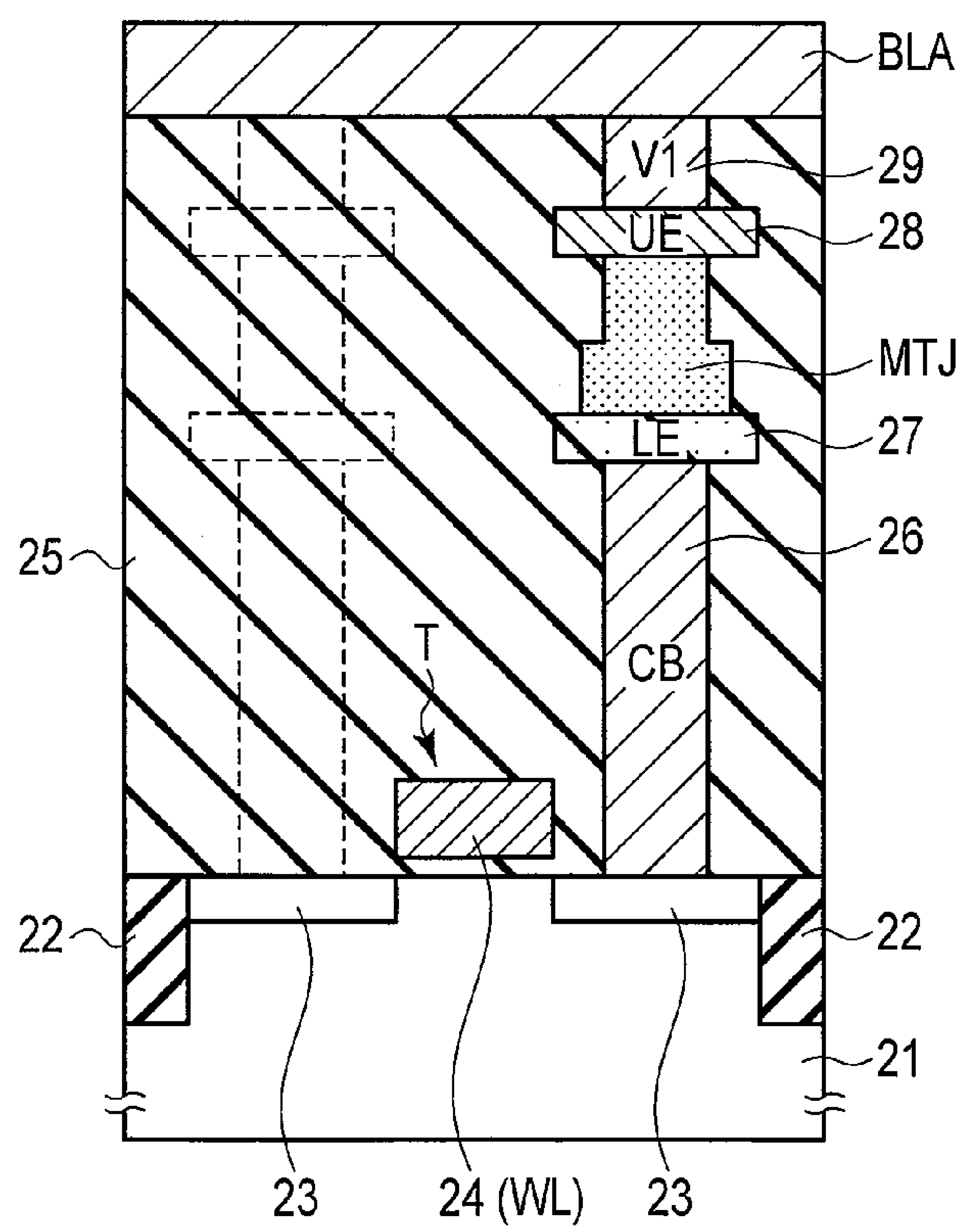


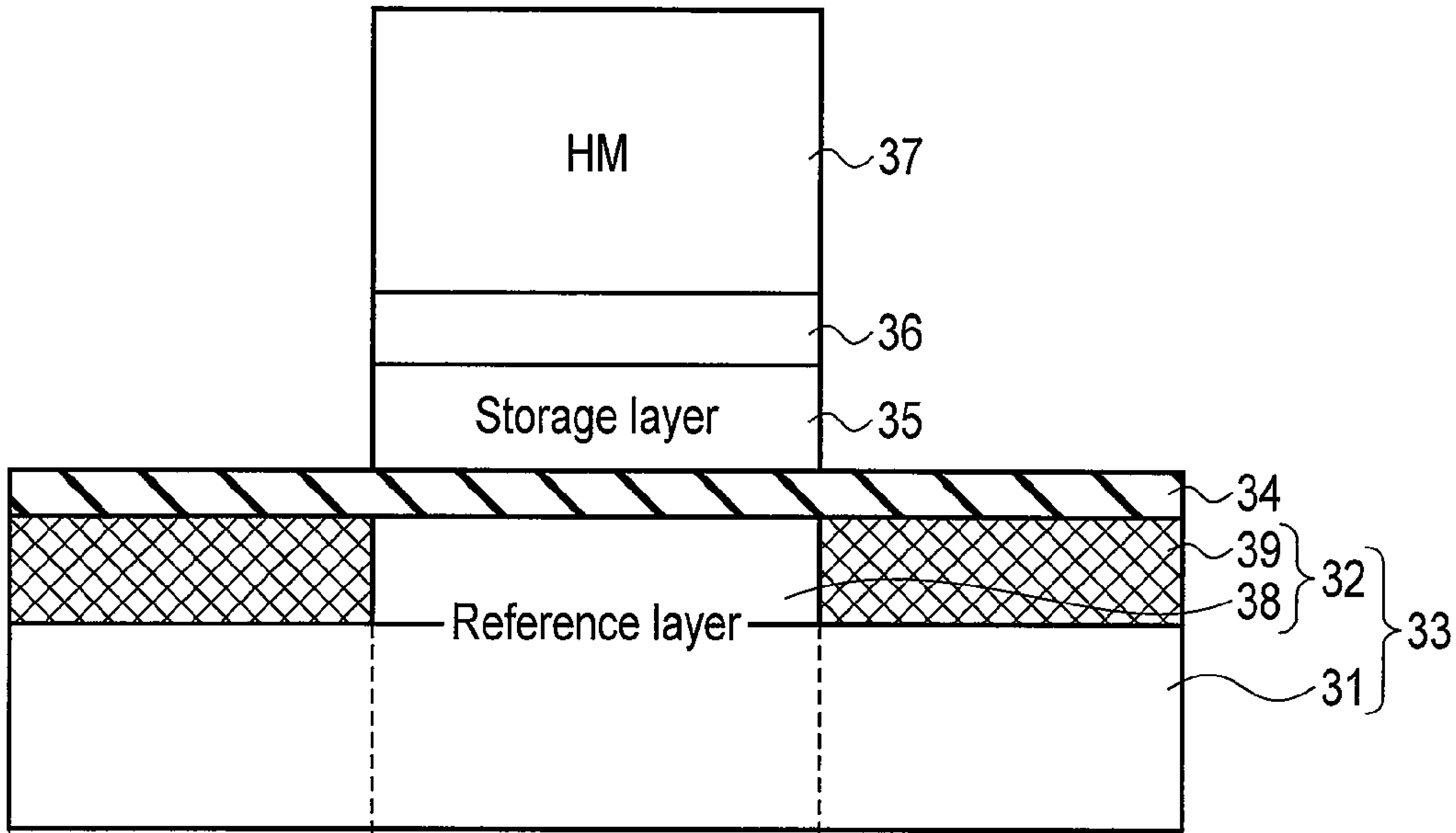
12
Second control circuit
WL
BLA
MTJ
T
MA
BLB
First control circuit
11

F I G. 1

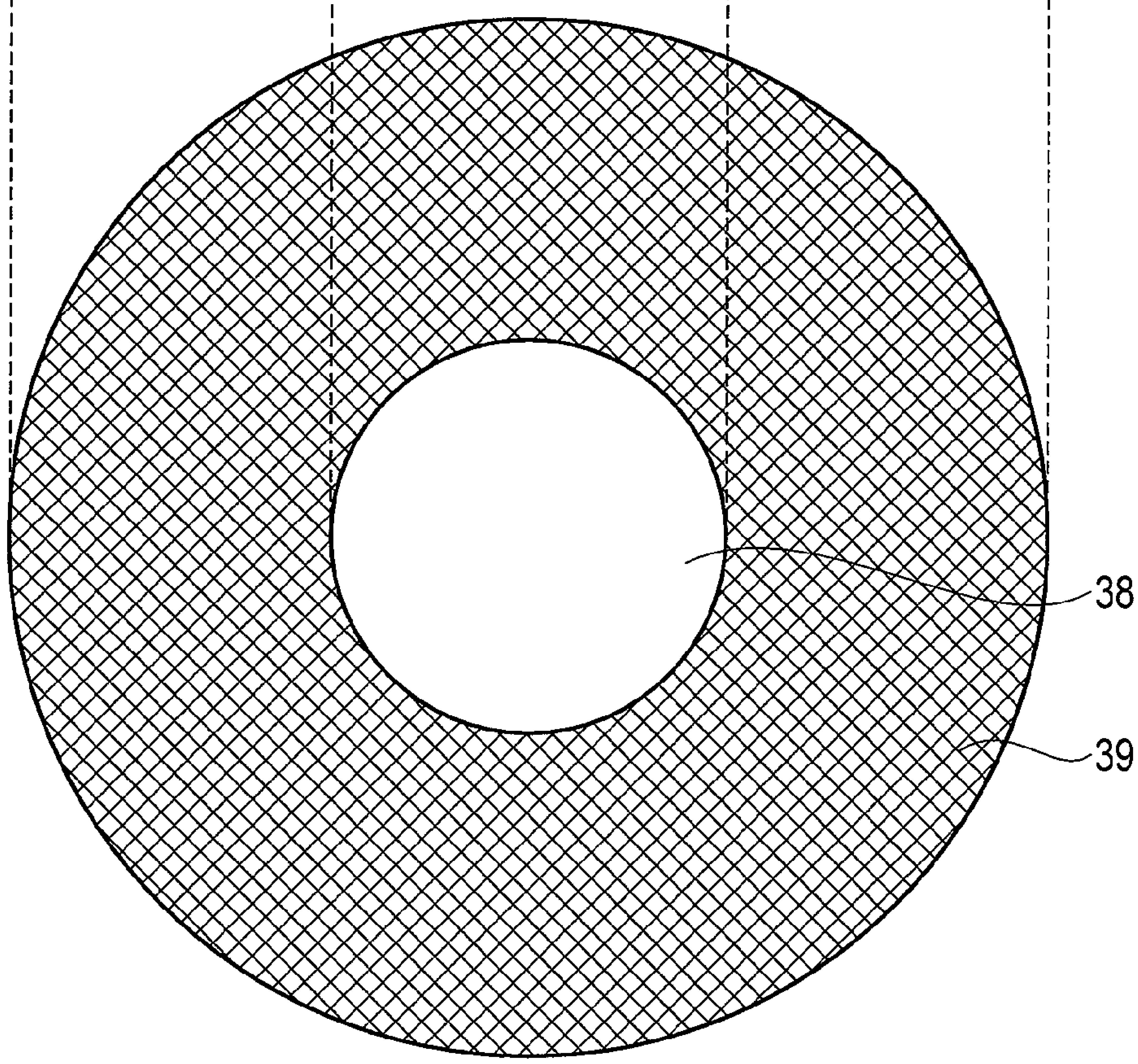


BLA
V1
29
UE
28
MTJ
LE
27
25
26
T
CB
22
22
21
23
24 (WL)
23

F I G. 2

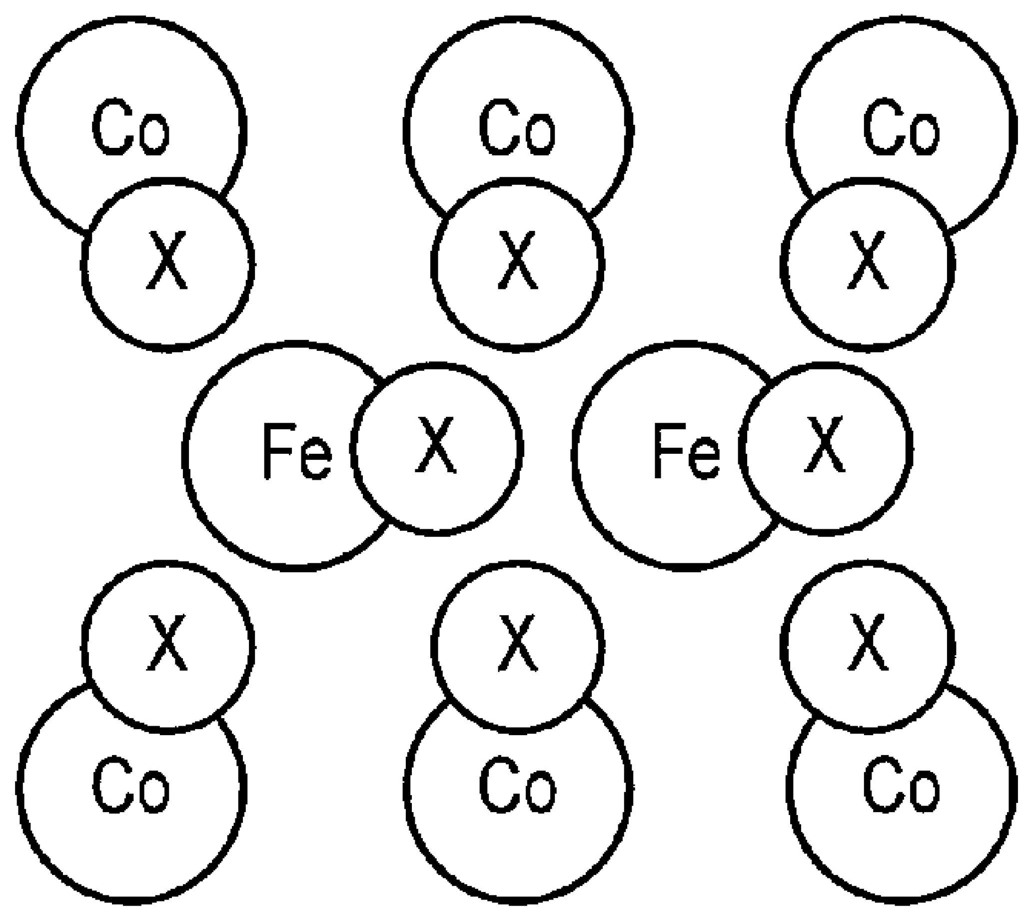

HM
37
36
Storage layer
35
34
39
38
32
33
Reference layer
31

F I G. 3 A


38
39

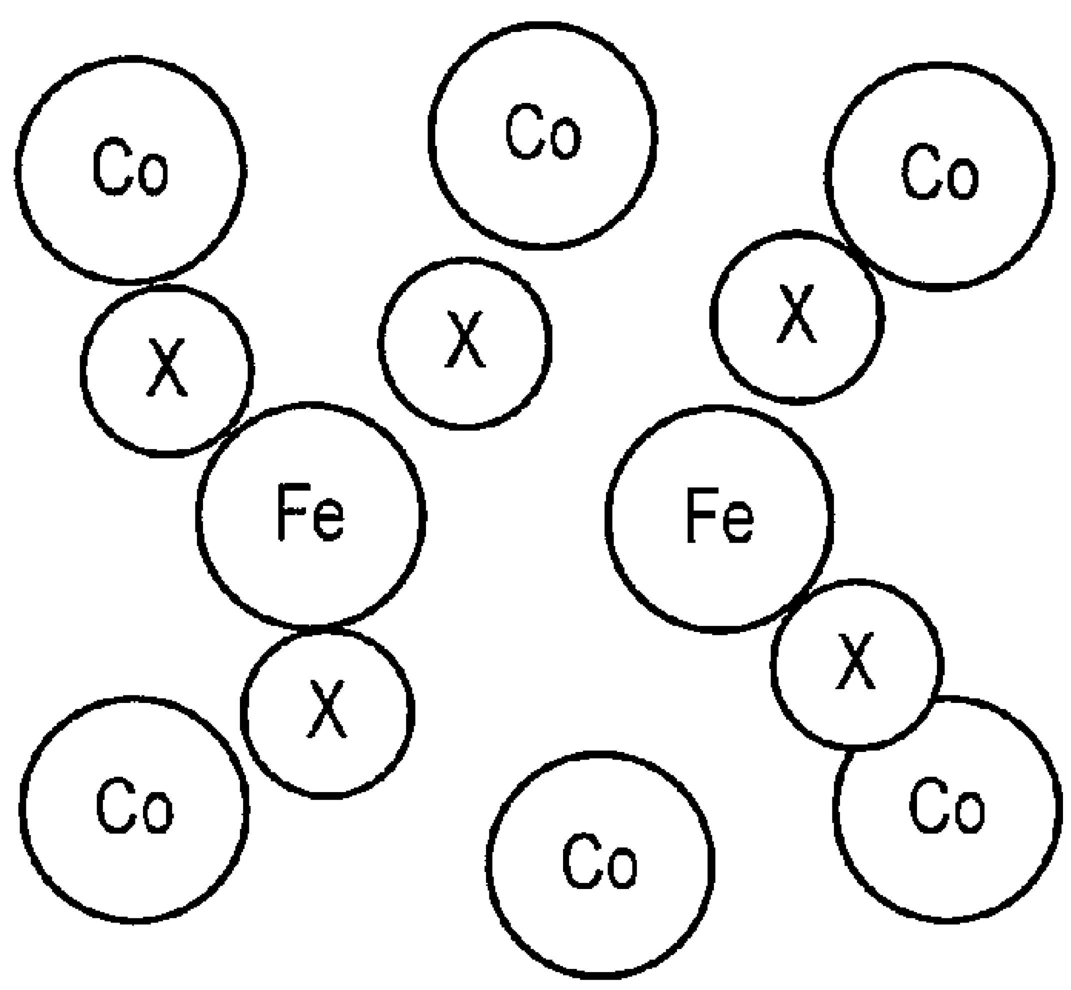
F I G. 3 B

Compound formation



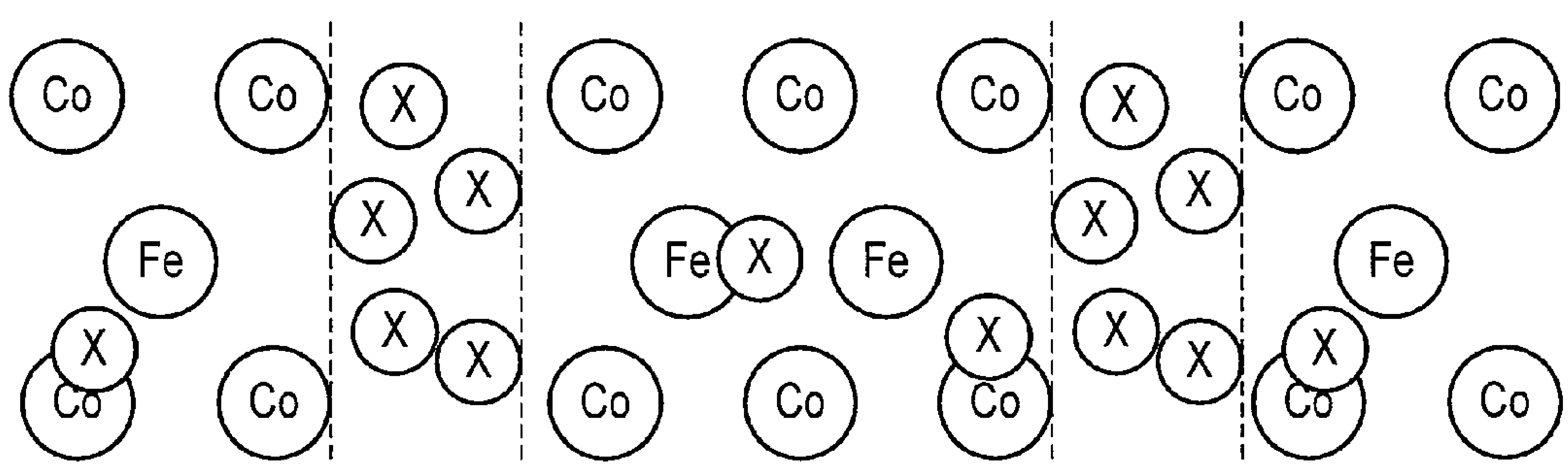
F I G. 4

Entry among lattice



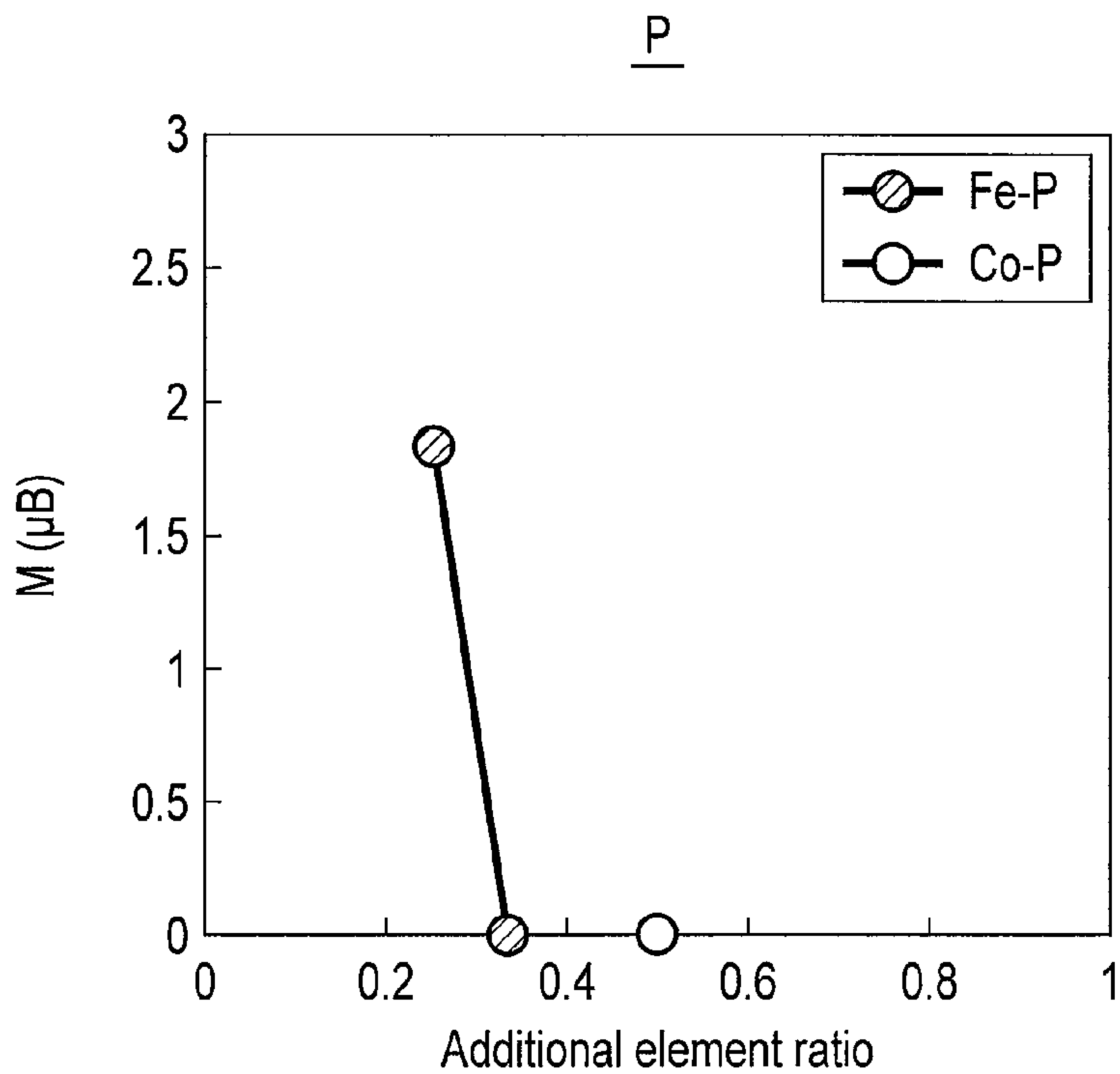
Interatomic distance prolongation

F I G. 5 A

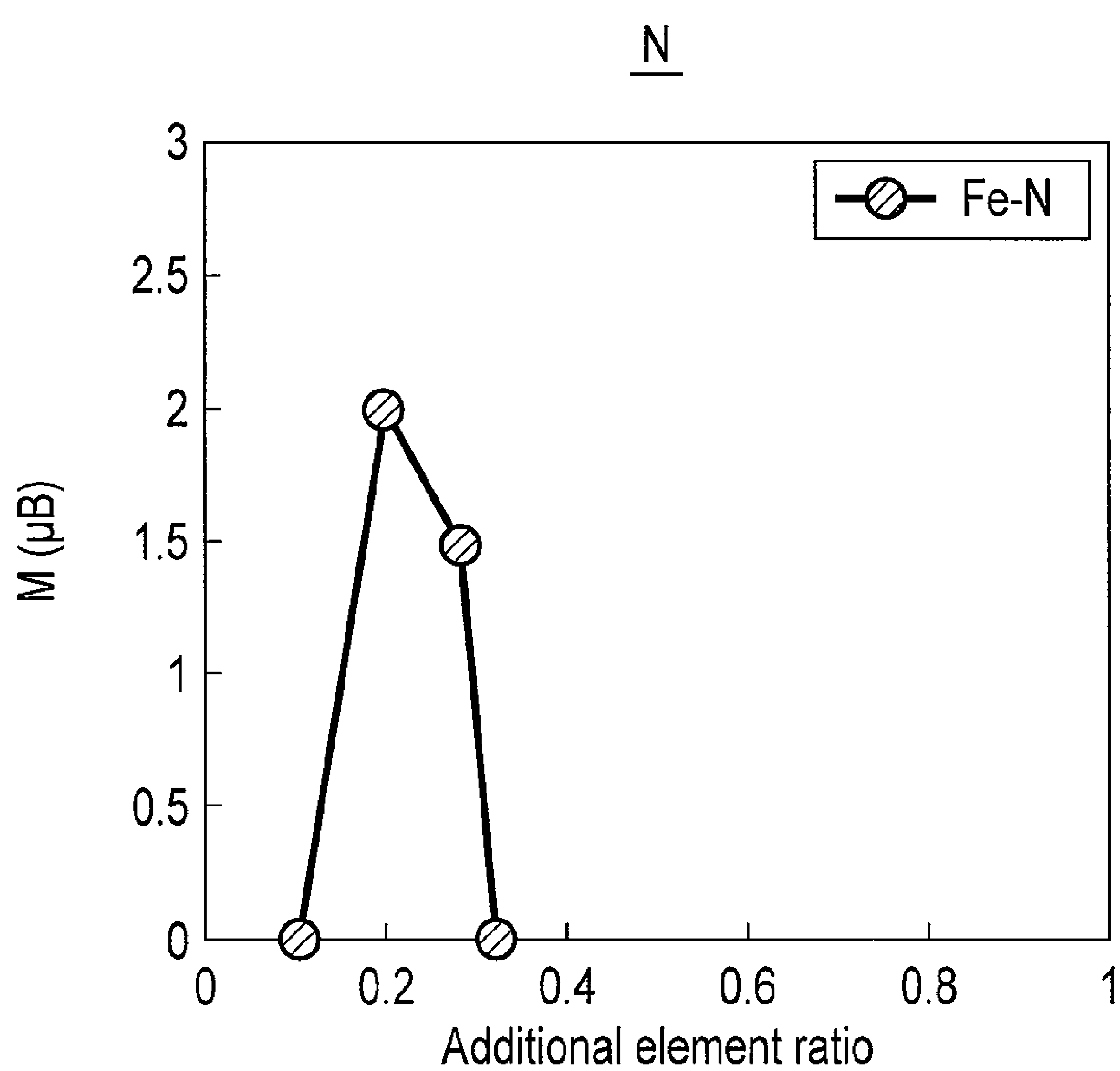


Magnetic cluster separation

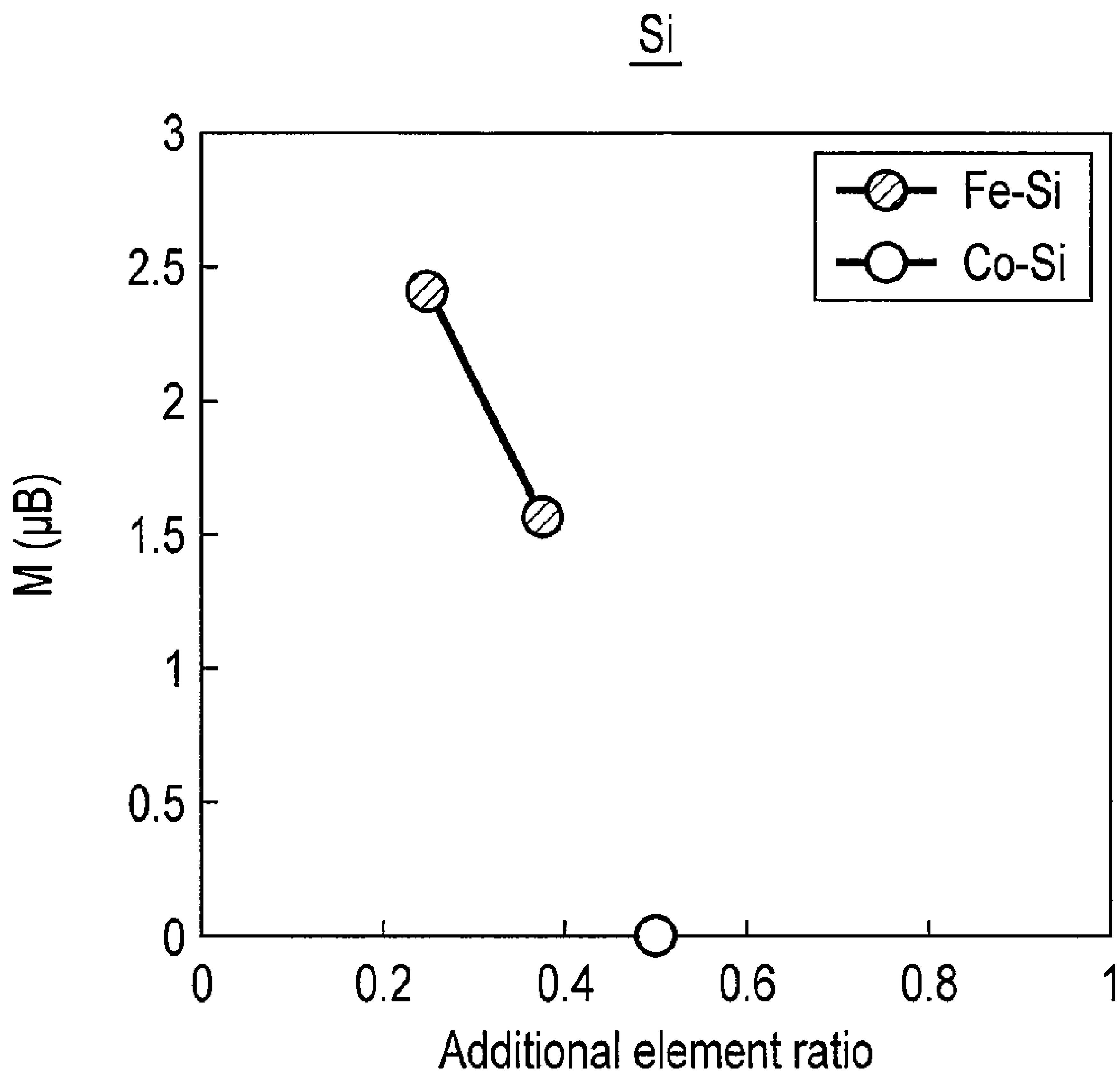
F I G. 5 B


P
Fe-P
Co-P
M (μB)
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
Additional element ratio

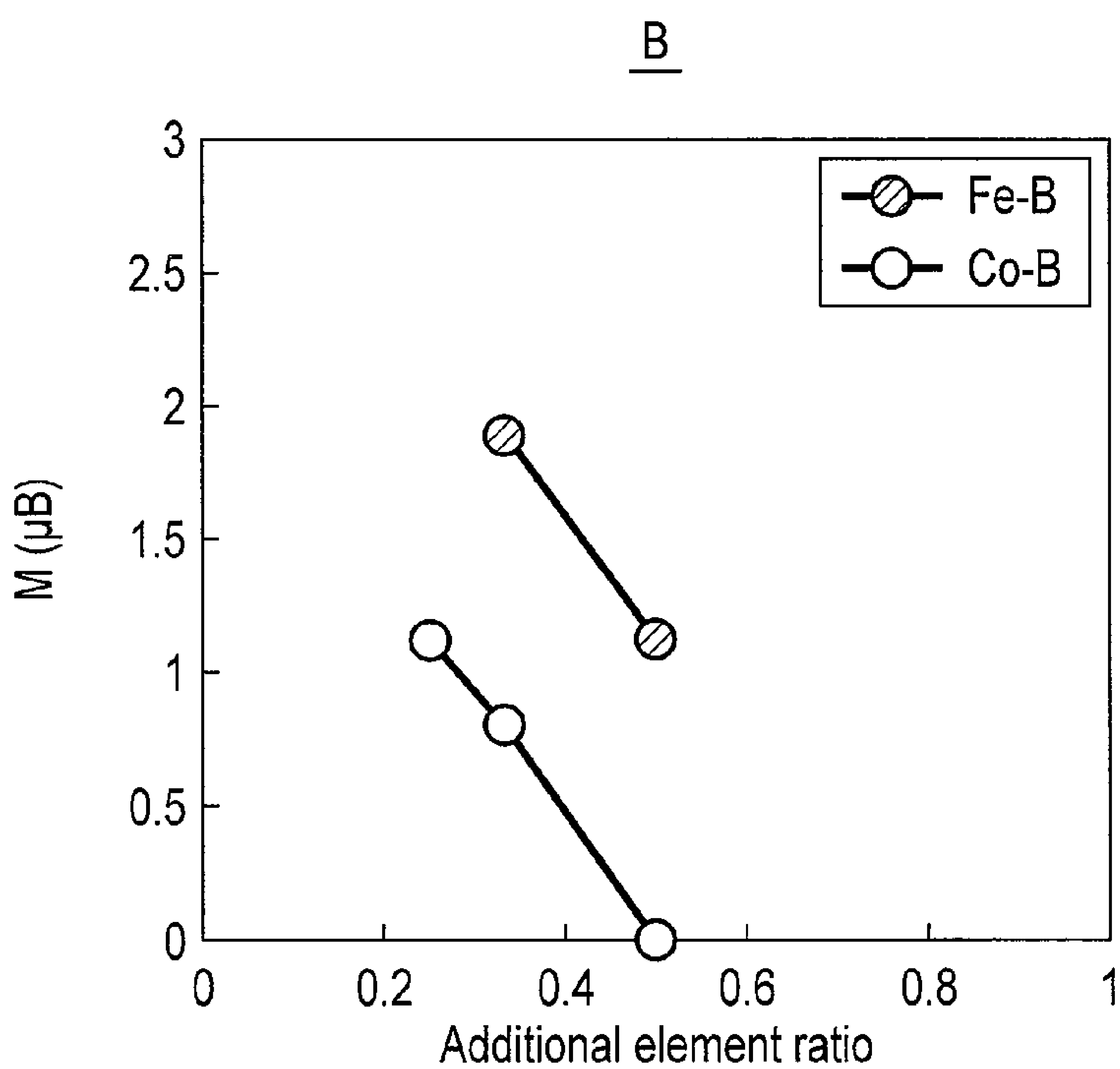
F I G. 6


N
Fe-N
M (μB)
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
Additional element ratio

F I G. 7


Si
Fe-Si
Co-Si
M (μB)
Additional element ratio
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1

F I G. 8


B
Fe-B
Co-B
M (μB)
Additional element ratio
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1

F I G. 9

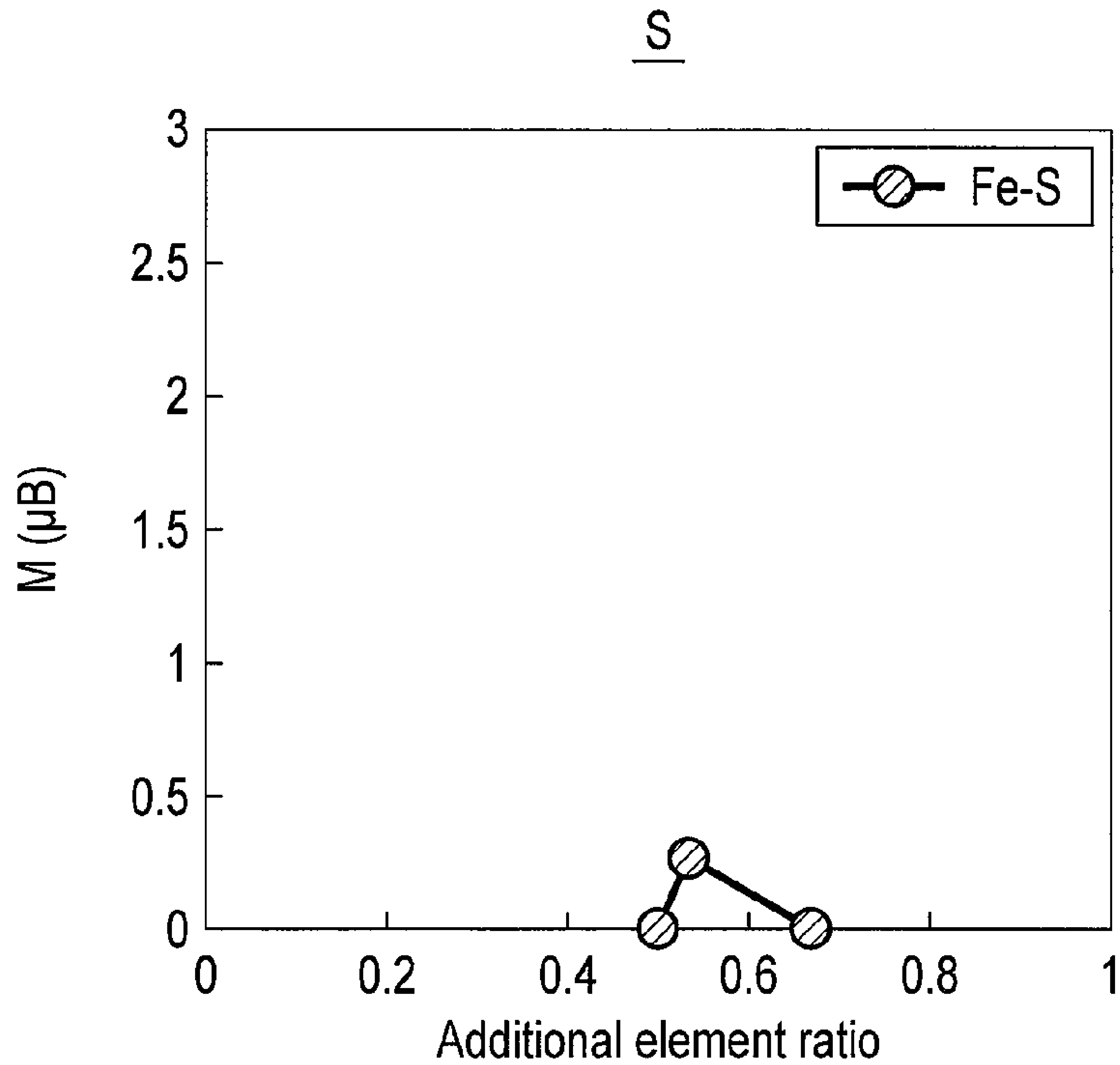

S
Fe-S
M (μB)
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
Additional element ratio

FIG. 10

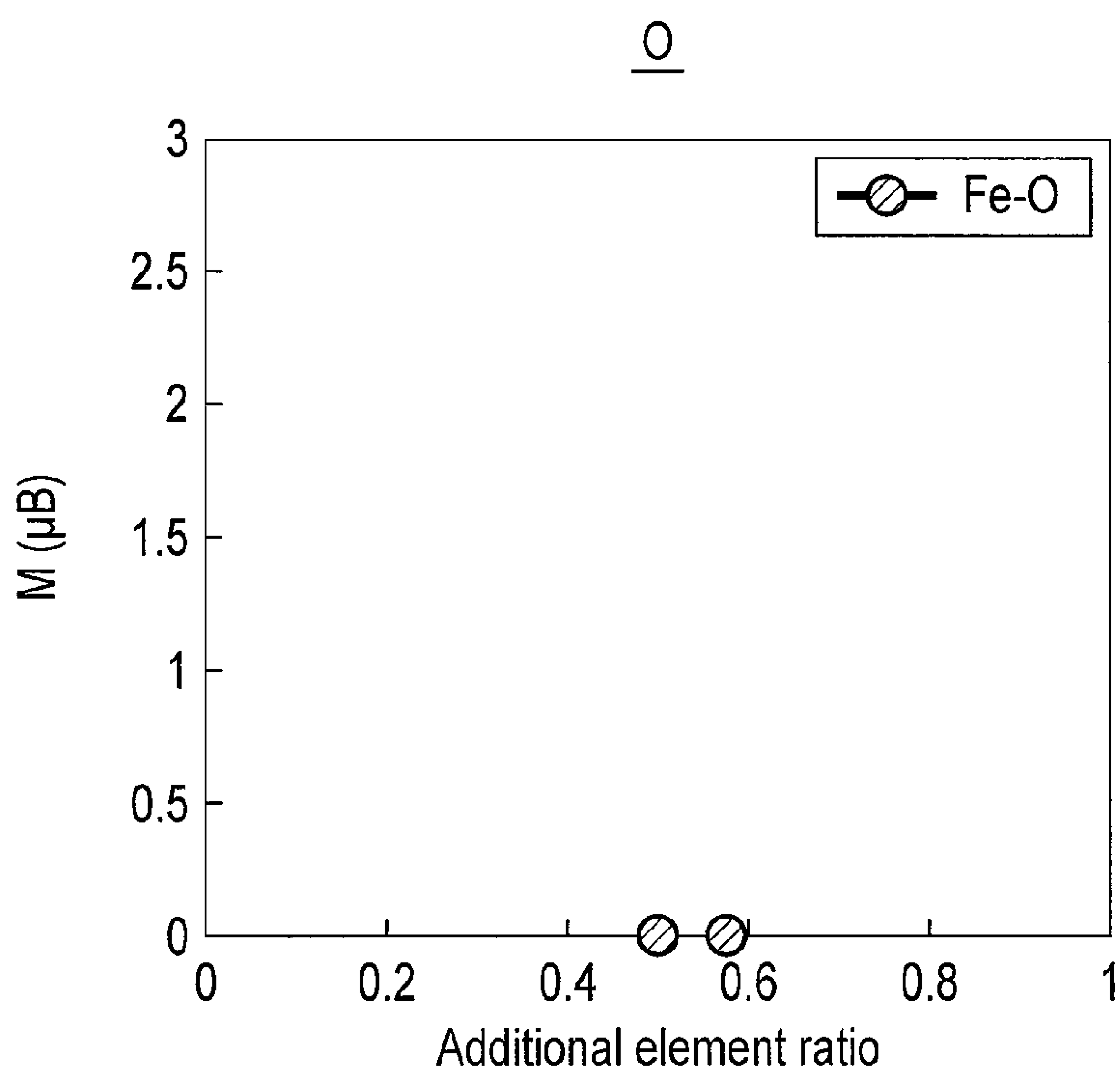
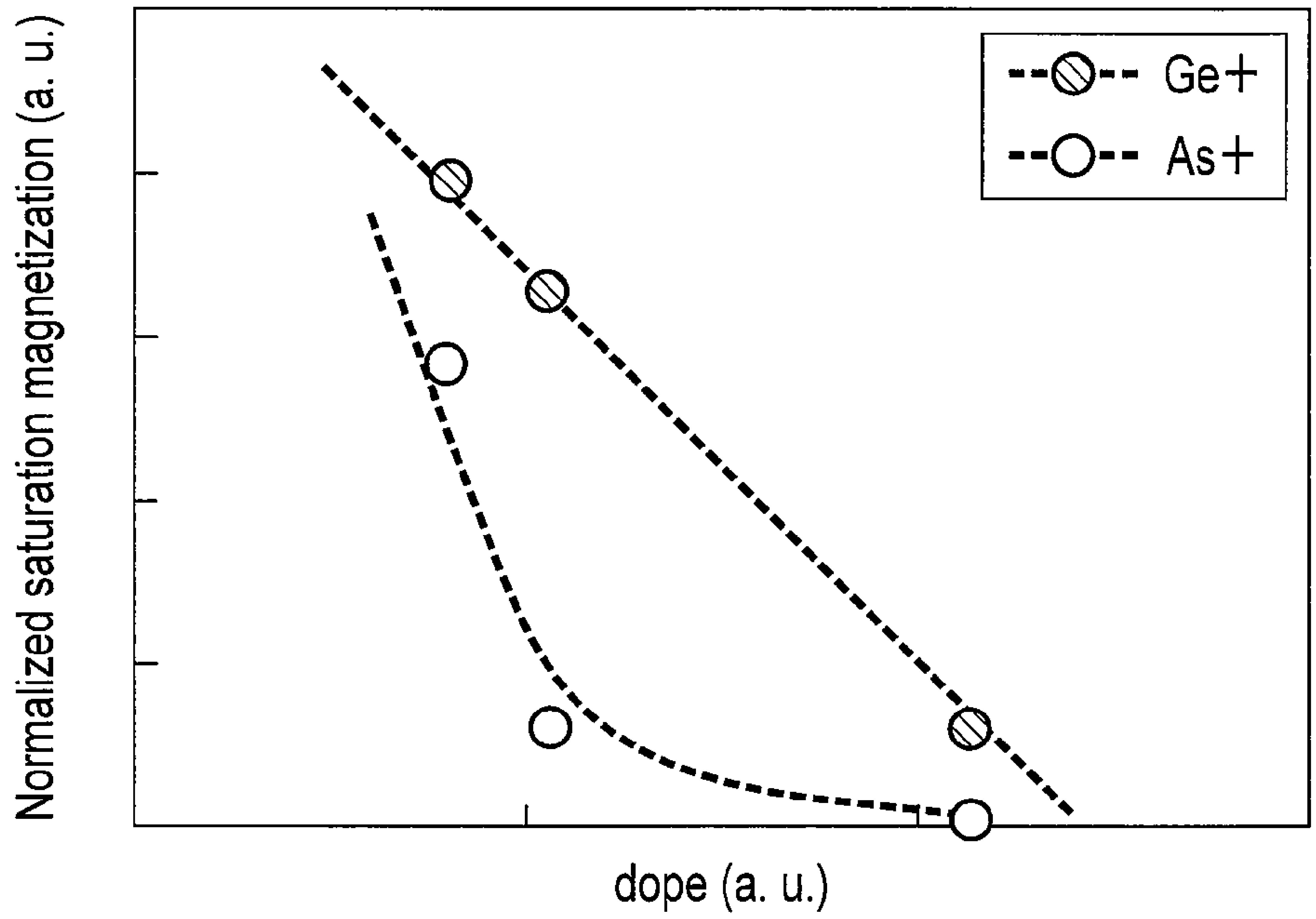
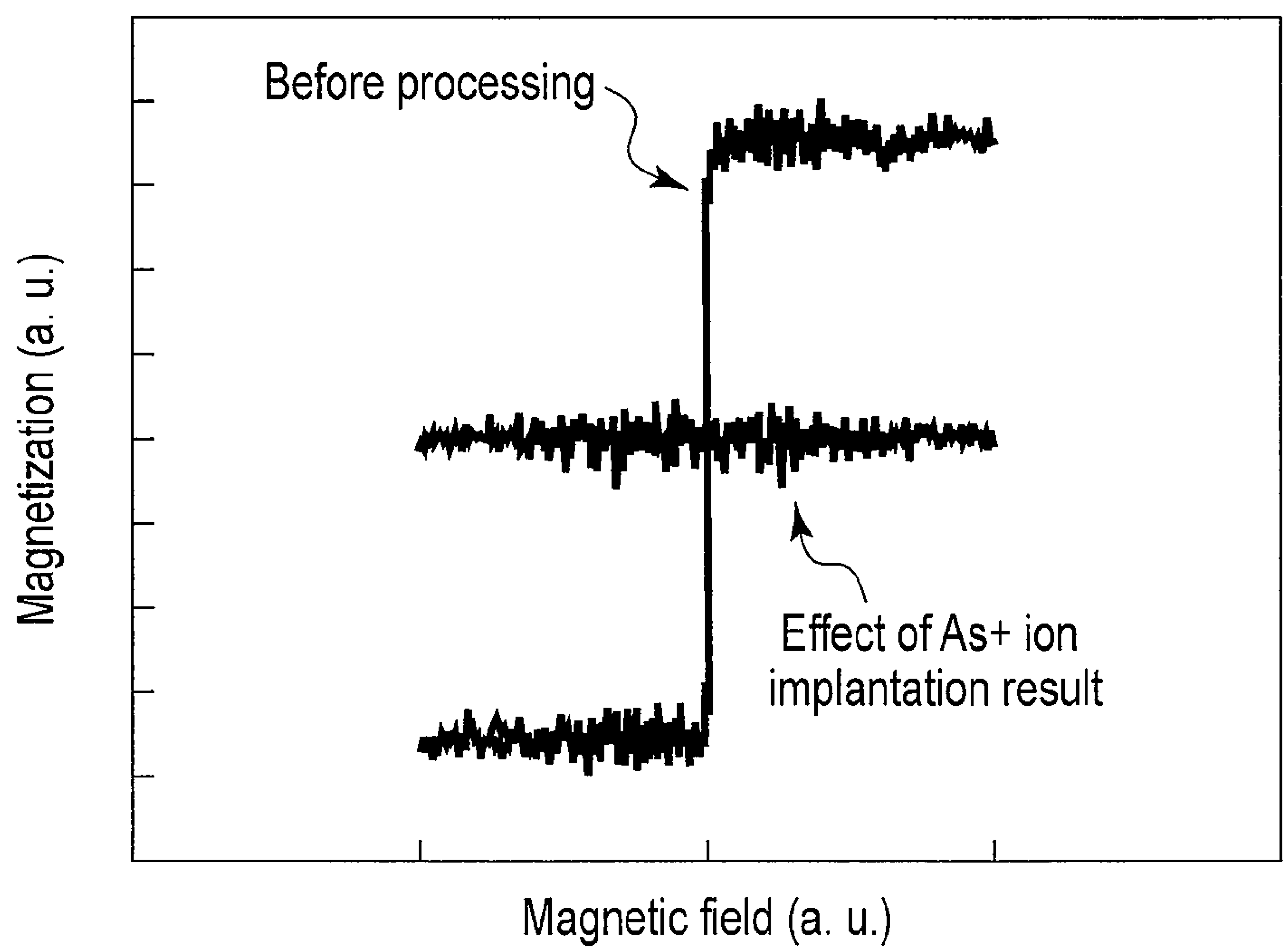

O
Fe-O
M (μB)
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
Additional element ratio

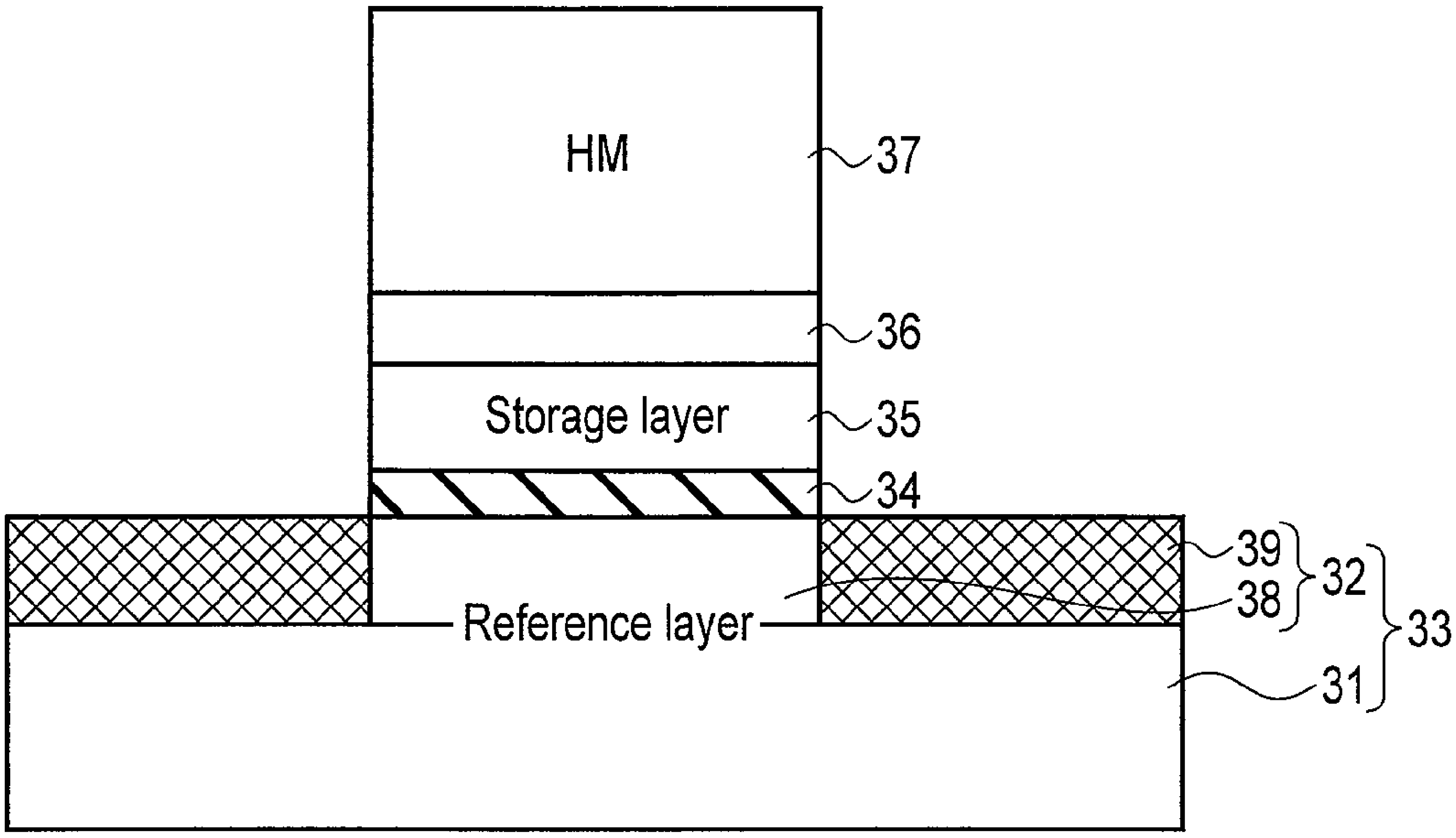
FIG. 11


Ge+
As+
Normalized saturation magnetization (a. u.)
dope (a. u.)

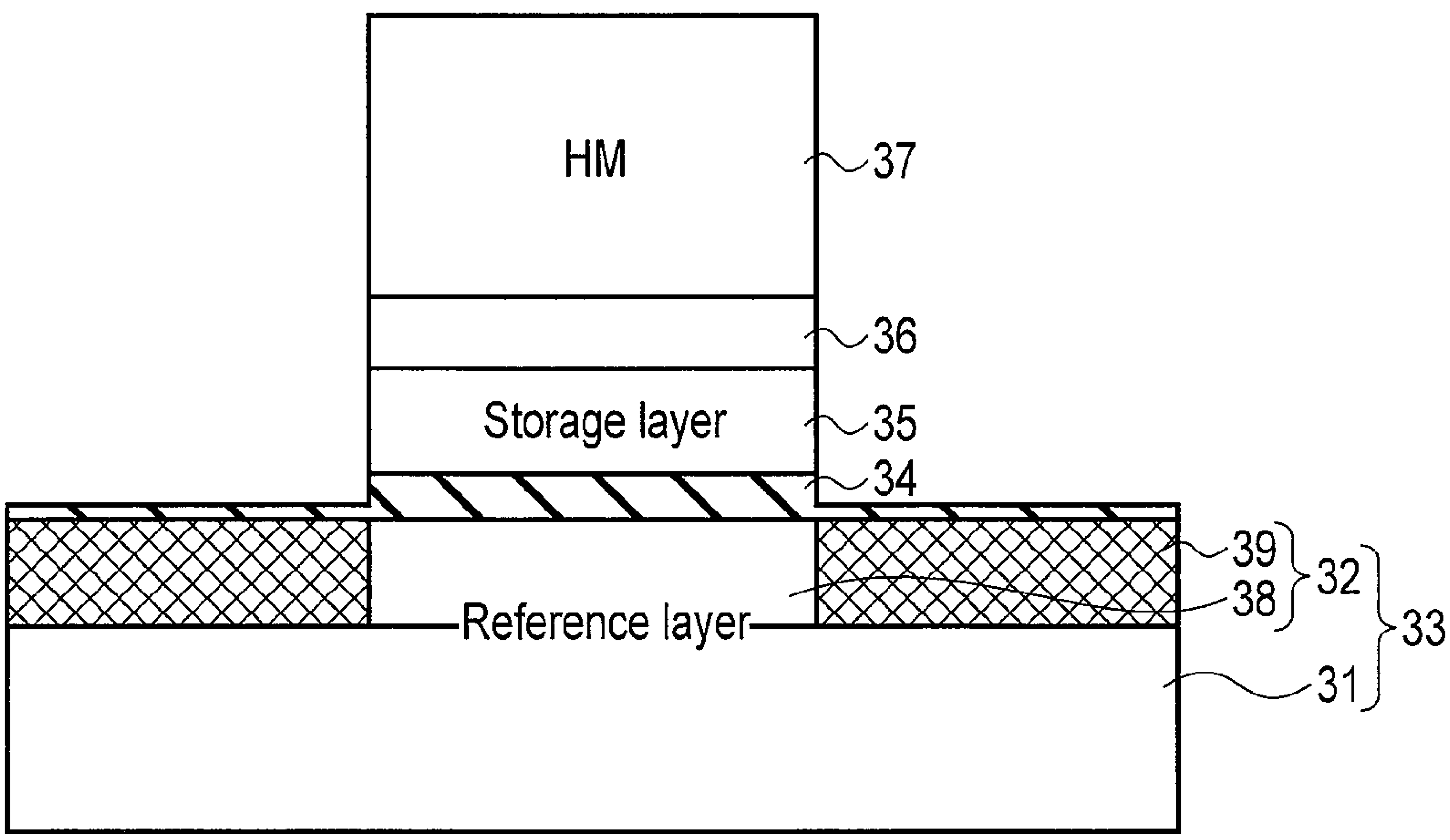
F I G. 1 2


Before processing
Effect of As+ ion implantation result
Magnetization (a. u.)
Magnetic field (a. u.)

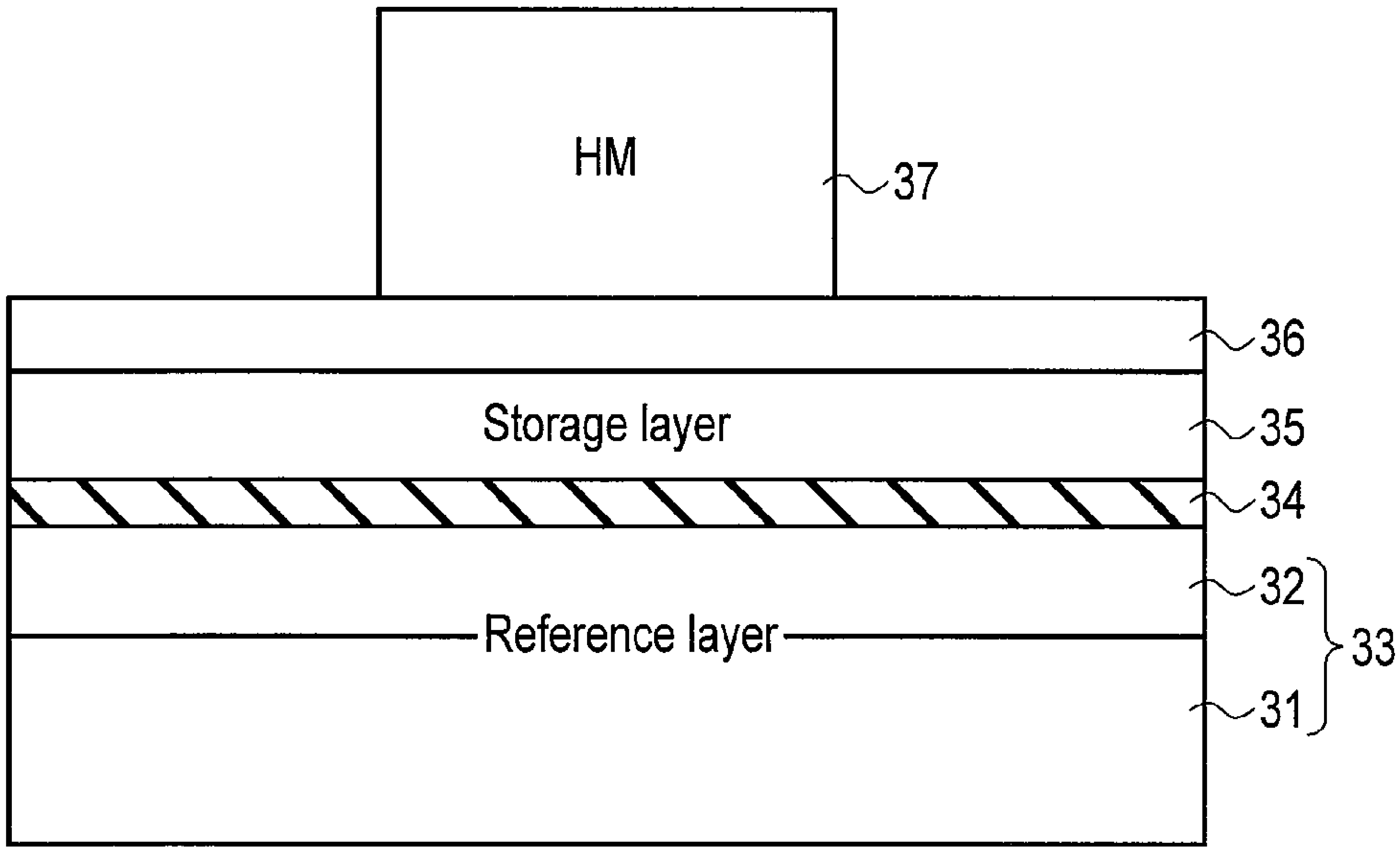
F I G. 1 3


HM
37
36
Storage layer
35
34
39
32
38
33
Reference layer
31

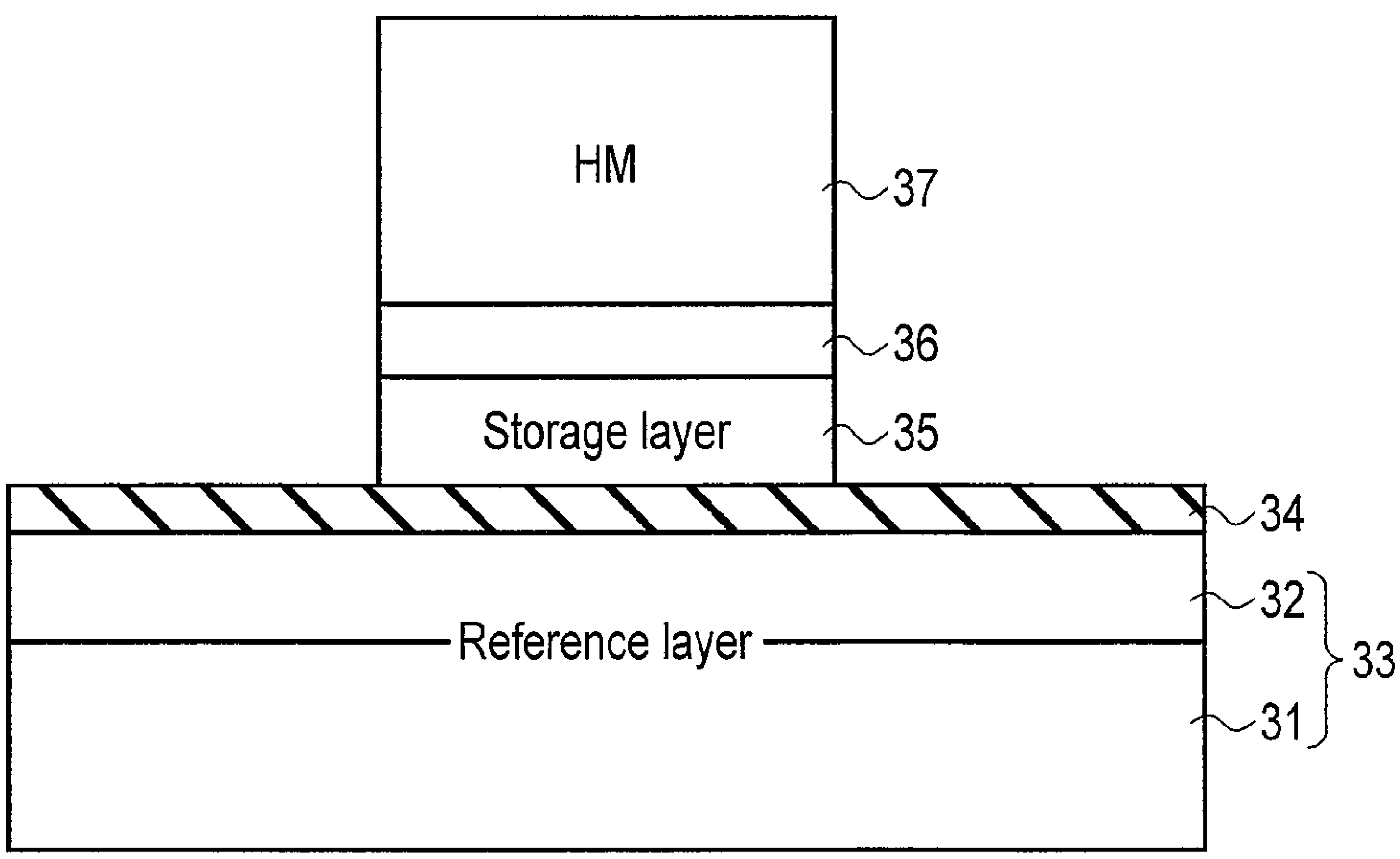
F I G. 1 4


HM
37
36
Storage layer
35
34
39
32
38
33
Reference layer
31

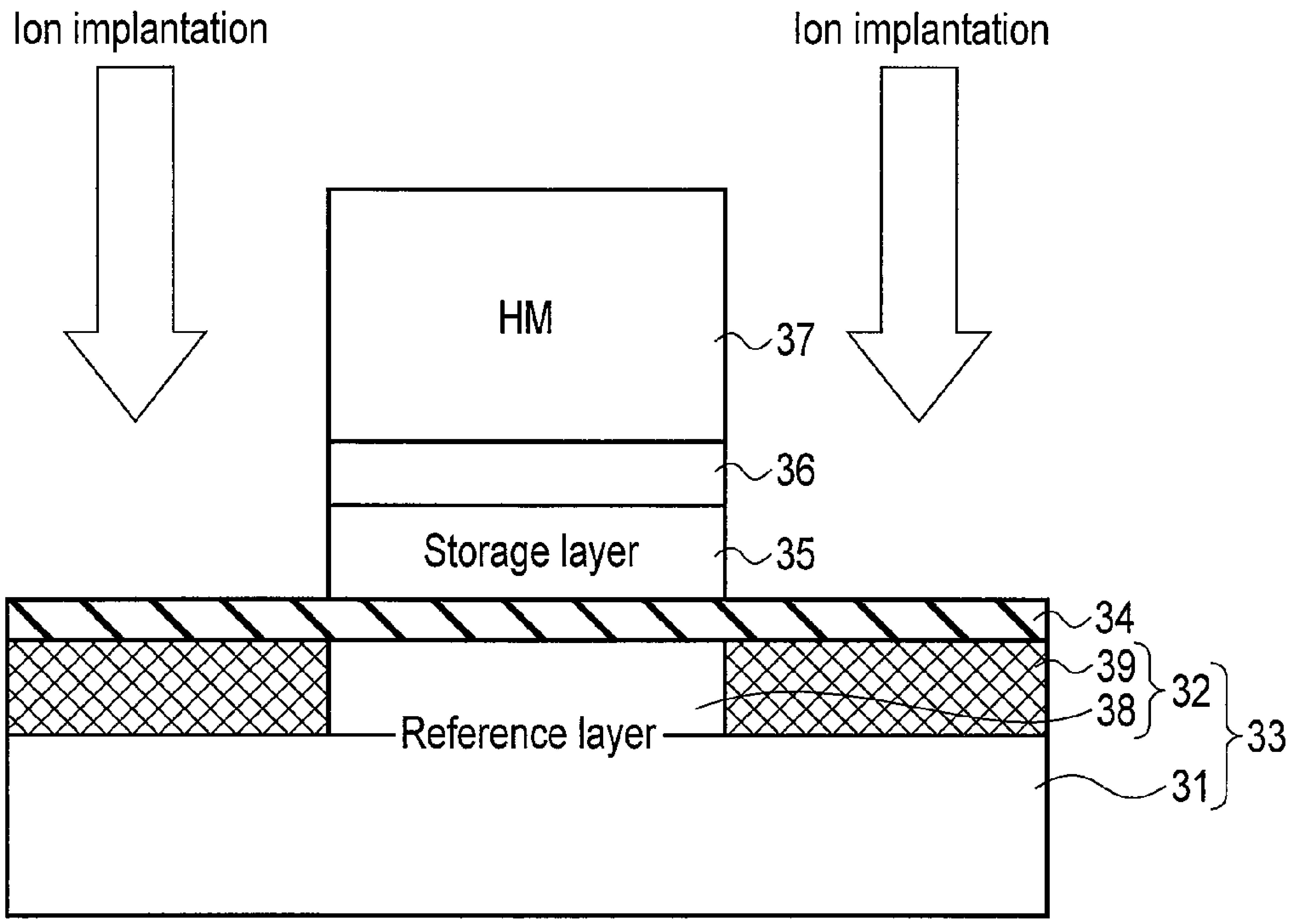
F I G. 1 5


HM
37
36
Storage layer
35
34
32
Reference layer
33
31

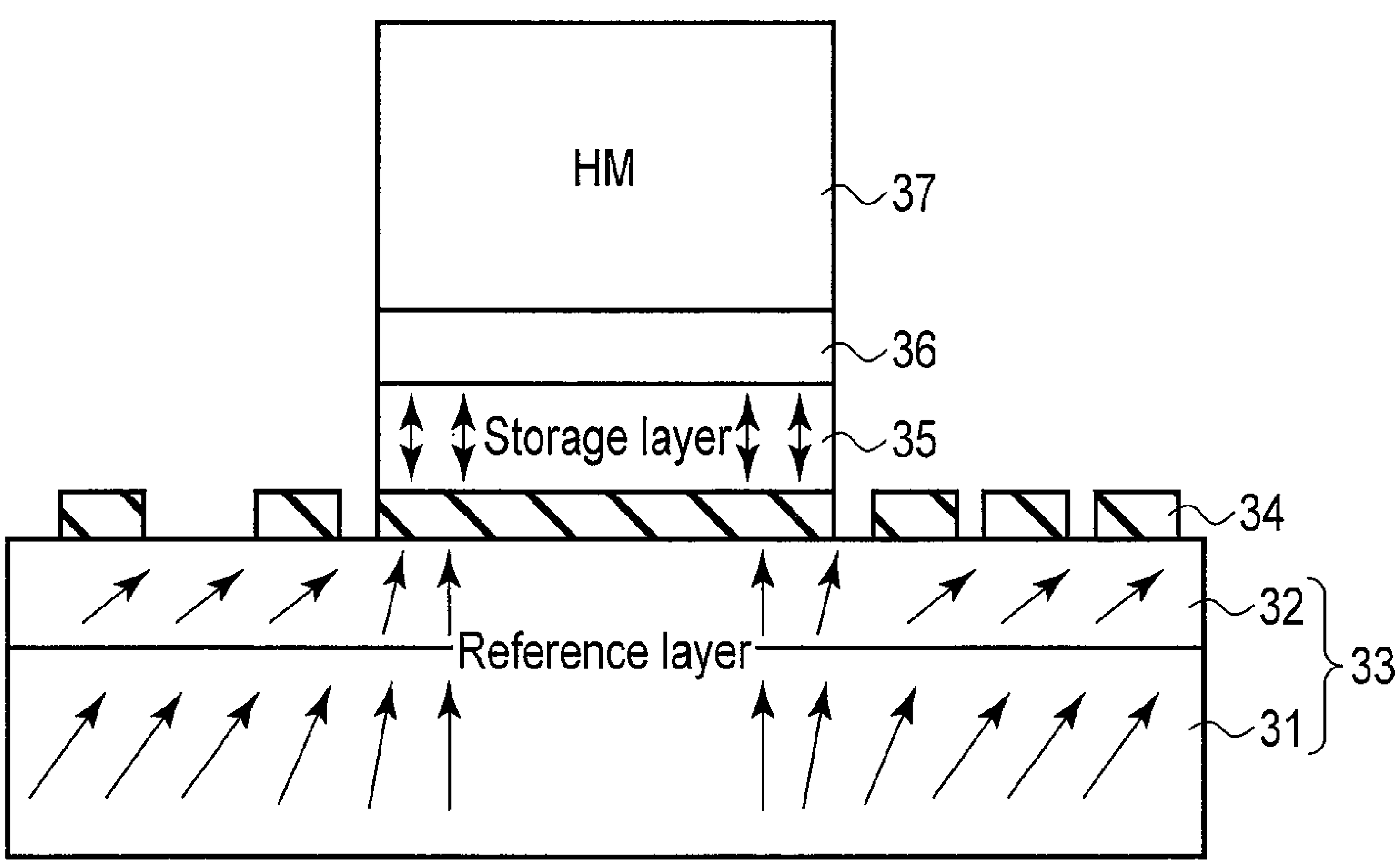
F I G. 1 6


HM
37
36
Storage layer
35
34
32
Reference layer
33
31

F I G. 1 7


Ion implantation
Ion implantation
HM
37
36
Storage layer
35
34
39
32
38
33
Reference layer
31

F I G. 1 8


HM
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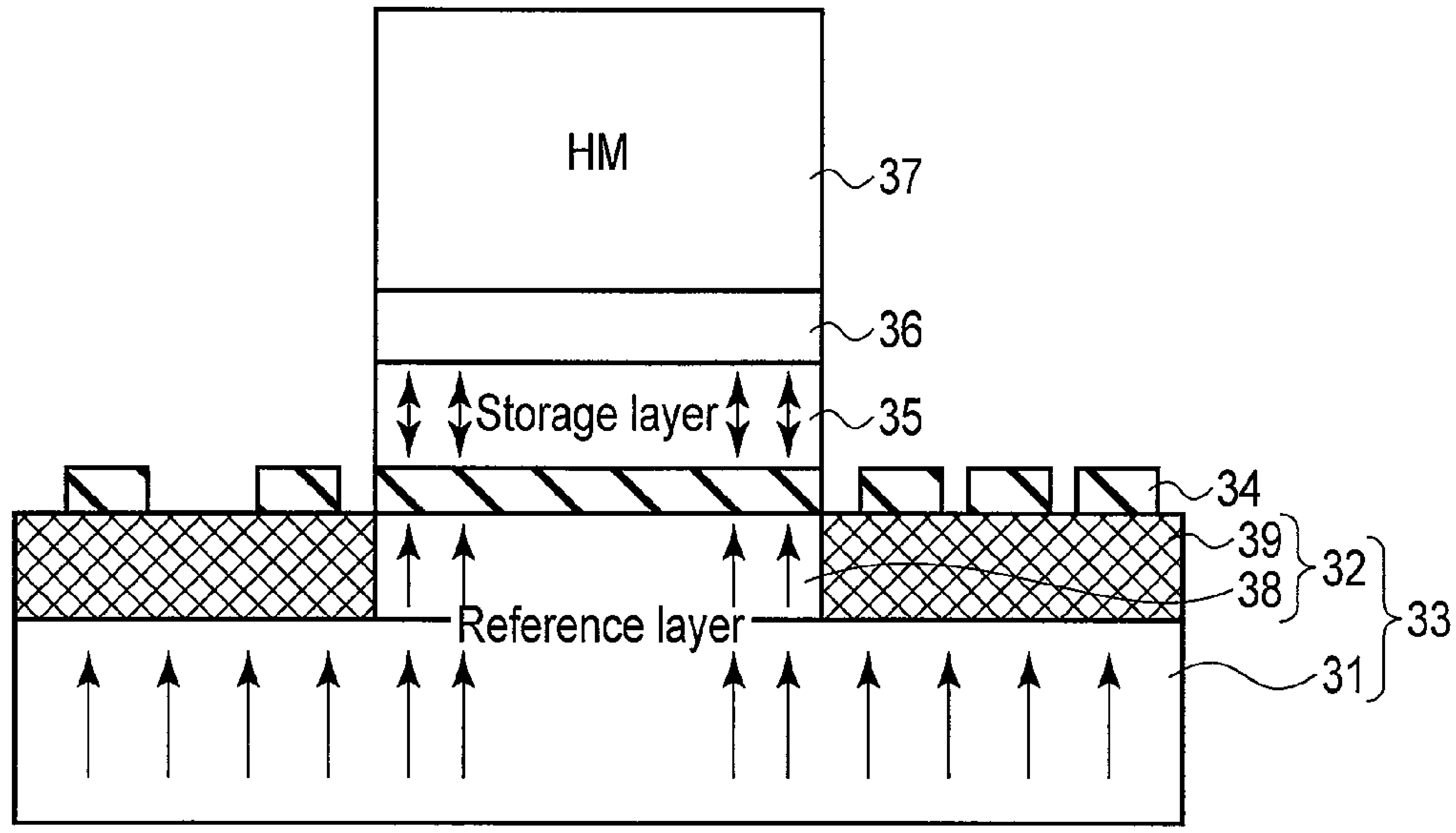
Storage layer
35
34
32
33
Reference layer
31

F I G. 1 9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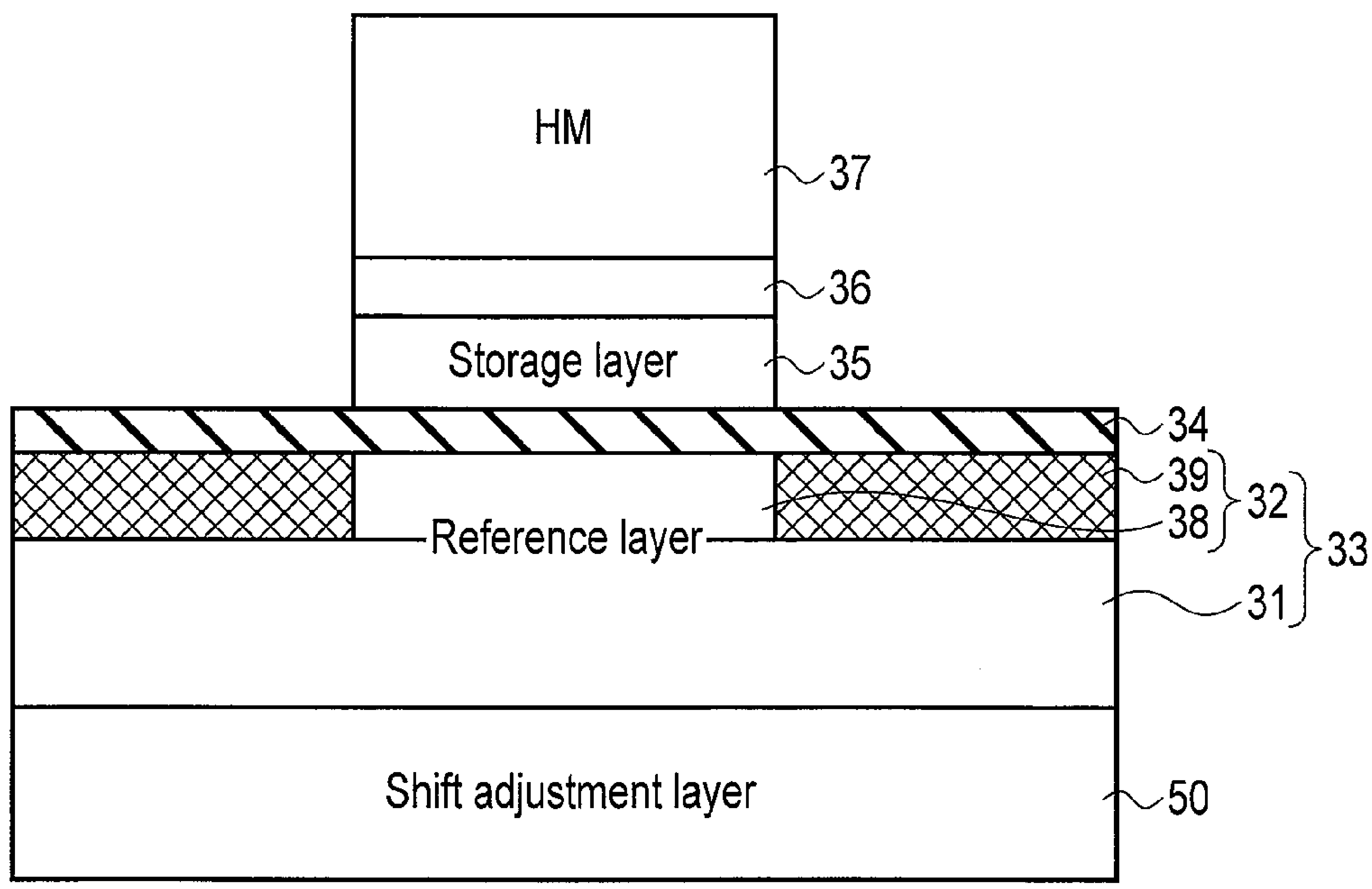
32
38
33
Reference layer
31

F I G. 2 0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Storage layer
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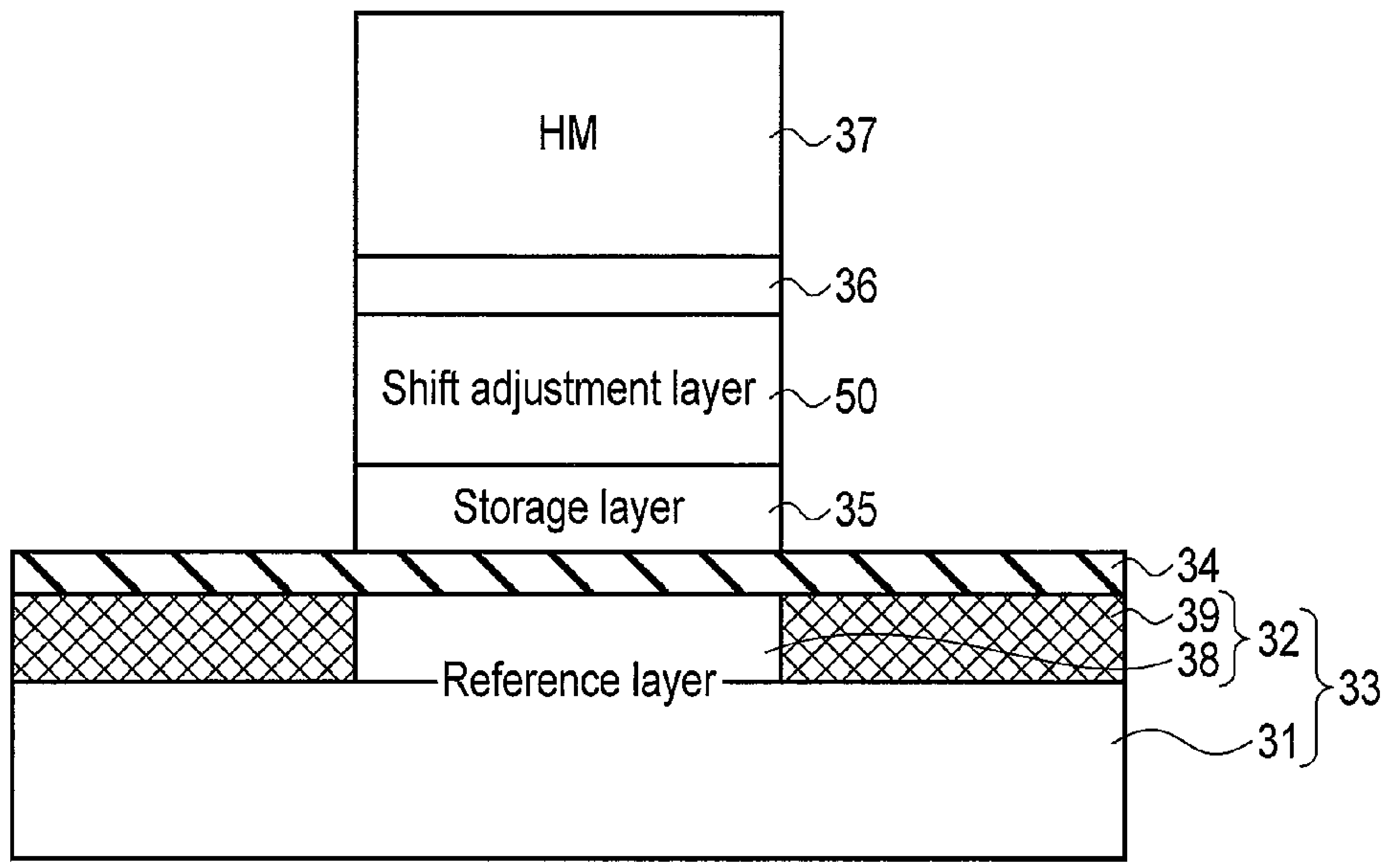
34
39
32
38
33
Reference layer
31
Shift adjustment layer
50

F I G. 2 1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36
Shift adjustment layer
50
Storage layer
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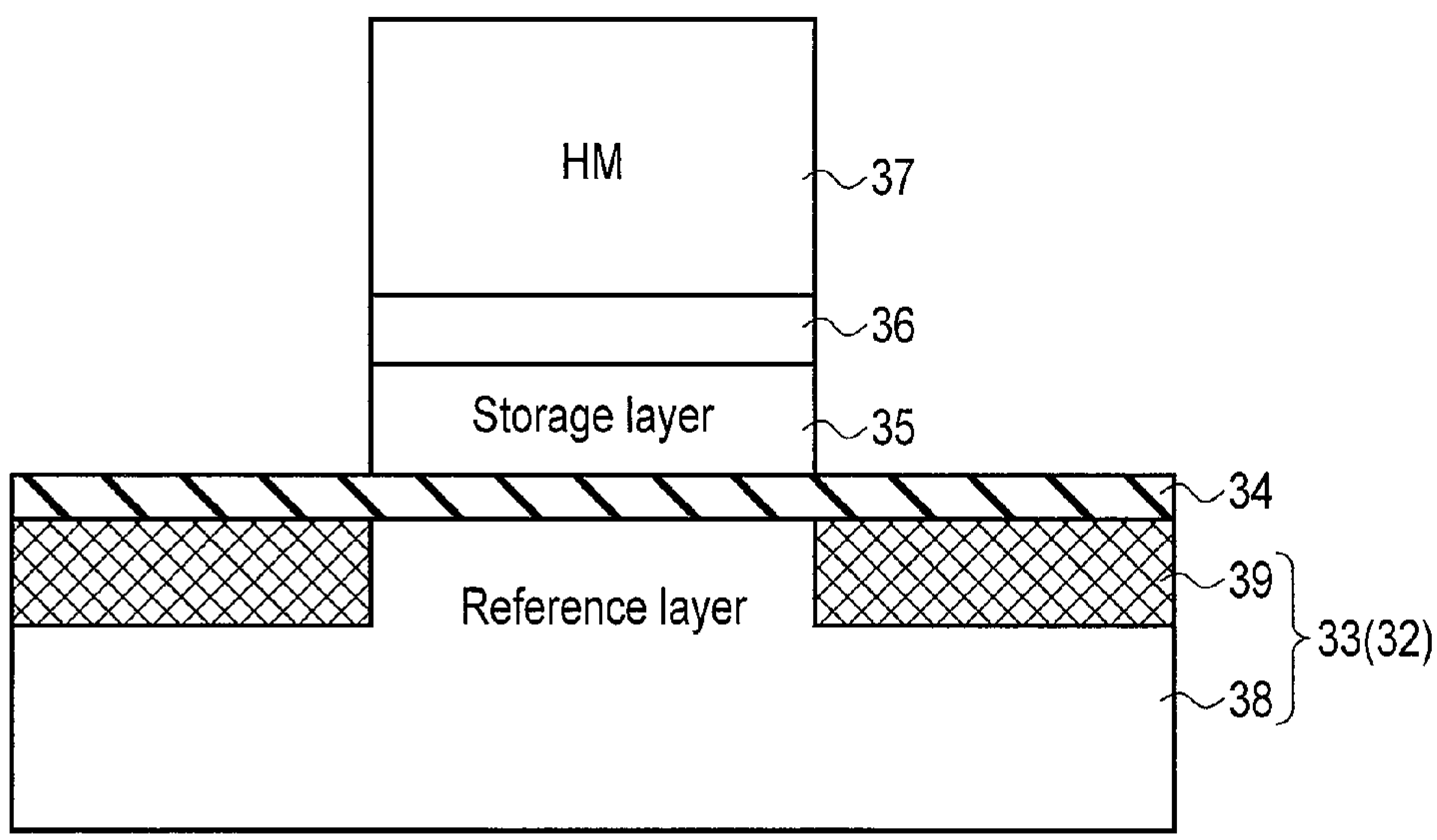
34
39
32
38
33
Reference layer
31

F I G. 2 2


HM
37
36
Storage layer
35
34
39
Reference layer
33(32)
38

F I G. 2 3

MAGNETORESISTIVE ELEMENT AND METHOD OF MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2011-205323, filed Sep. 20, 2011, the entire contents of which are incorporated herein by reference.

FIELD

Embodiments described herein relate generally to a magnetoresistive element and method of manufacturing the same.

BACKGROUND

An MRAM (Magnetic Random Access Memory) using a ferromagnetic material is expected as a nonvolatile memory endowed with nonvolatileness, high operation speed, large capacity, and low power consumption. The MRAM includes MTJ (Magnetic Tunnel Junction) elements using the TMR (Tunneling MagnetoResistive) effect as memory elements, and stores information based on the magnetization states of the MTJ elements. A perpendicular magnetization MTJ element has been proposed as an MTJ element, which stores information by generating magnetization perpendicular to the film surface.

The MTJ element includes a storage layer having a variable magnetization direction, and a reference layer having an invariable magnetization direction. The storage layer is stacked on a tunnel barrier layer on the reference layer. In the perpendicular magnetization MTJ element, the reference layer and the storage layer have different sizes. More specifically, the reference layer has, on the plane, a diameter larger than that of the storage layer located above. That is, the MTJ element has a step shape in the section. The reference layer includes an interface layer having a high polarization rate near the interface to the tunnel barrier layer to obtain a high magnetoresistive ratio necessary for reading information.

In general, perpendicular magnetic anisotropy is generated in the interface between the tunnel barrier layer and the interface layer. However, in the process of forming the above-described step structure, the tunnel barrier layer having an exposed surface is nonuniformly etched, and the crystal structure is distorted. Hence, the perpendicular magnetic anisotropy of the interface layer disappears, and the perpendicular magnetic anisotropy of the reference layer becomes unstable.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a circuit diagram showing a memory cell of an MRAM according to each embodiment;

FIG. **2** is a sectional view showing the structure of the memory cell of the MRAM according to each embodiment;

FIGS. **3**A and **3**B shows the structure of a magnetoresistive element MTJ according to the first embodiment;

FIG. **4** is a view showing an example of the principle of magnetization disappearance of a deactivated area according to the first embodiment;

FIGS. **5**A and **5**B is views showing other examples of the principle of magnetization disappearance of the deactivated area according to the first embodiment;

FIG. **6** is a graph showing the relationship between magnetization and the additional element ratio of a P element when the P element is doped into the deactivated area according to the first embodiment;

FIG. **7** is a graph showing the relationship between magnetization and the additional element ratio of an N element when the N element is doped into the deactivated area according to the first embodiment;

FIG. **8** is a graph showing the relationship between magnetization and the additional element ratio of an Si element when the Si element is doped into the deactivated area according to the first embodiment;

FIG. **9** is a graph showing the relationship between magnetization and the additional element ratio of a B element when the B element is doped into the deactivated area according to the first embodiment;

FIG. **10** is a graph showing the relationship between magnetization and the additional element ratio of an S element when the S element is doped into the deactivated area according to the first embodiment;

FIG. **11** is a graph showing the relationship between magnetization and the additional element ratio of an O element when the O element is doped into the deactivated area according to the first embodiment;

FIG. **12** is a graph showing the relationship between the doping amount and magnetization when a group IV element and a group V element are doped into the deactivated area according to the first embodiment;

FIG. **13** is a graph showing the relationship between the magnetic field and magnetization when a group V element is doped into the deactivated area according to the first embodiment and a comparative example;

FIG. **14** is a sectional view showing the structure of a first modification of the magnetoresistive element MTJ according to the first embodiment;

FIG. **15** is a sectional view showing the structure of a second modification of the magnetoresistive element MTJ according to the first embodiment;

FIGS. **16**, **17**, and **18** are sectional views showing steps in the manufacture of the magnetoresistive element MTJ according to the first embodiment;

FIG. **19** is a sectional view showing a comparative example of the magnetization direction of the magnetoresistive element MTJ according to the first embodiment;

FIG. **20** is a sectional view showing the magnetization direction of the magnetoresistive element MTJ according to the first embodiment;

FIG. **21** is a sectional view showing the structure of a magnetoresistive element MTJ according to the second embodiment;

FIG. **22** is a sectional view showing the structure of a modification of the magnetoresistive element MTJ according to the second embodiment; and

FIG. **23** is a sectional view showing the structure of a magnetoresistive element MTJ according to the third embodiment.

DETAILED DESCRIPTION

In general, according to one embodiment, a magnetoresistive element comprises a first magnetic layer having a magnetization direction invariable and perpendicular to a film surface, a tunnel barrier layer formed on the first magnetic layer, and a second magnetic layer formed on the tunnel barrier layer and having a magnetization direction variable and perpendicular to the film surface. The first magnetic layer includes an interface layer formed on an upper side in contact with a lower portion of the tunnel barrier layer, and a main body layer formed on a lower side and serving as an origin of perpendicular magnetic anisotropy. The interface layer includes a first area provided on an inner side and having magnetization, and a second area provided on an outer side to surround the first area and having magnetization smaller than the magnetization of the first area or no magnetization.

The embodiments will now be described with reference to the accompanying drawings. The same reference numerals denote the same parts throughout the drawings, and a repetitive description thereof will be done as needed.

1. Example of Arrangement of MRAM

An example of the arrangement of an MRAM according to each embodiment will be described with reference to FIGS. **1** and **2**.

FIG. **1** is a circuit diagram showing a memory cell of the MRAM according to each embodiment.

As shown in FIG. **1**, a memory cell in a memory cell array MA includes a series connection structure of a magnetoresistive element MTJ and a switch element (for example, FET) T. One terminal of the series connection structure (one terminal of the magnetoresistive element MTJ) is connected to a bit line BLA, and the other terminal of the series connection structure (one terminal of the switch element T) is connected to a bit line BLB. The control terminal of the switch element T, for example, the gate electrode of the FET is connected to a word line WL.

The potential of the word line WL is controlled by a first control circuit **11**. The potentials of the bit lines BLA and BLB are controlled by a second control circuit **12**.

FIG. **2** is a sectional view showing the structure of the memory cell of the MRAM according to each embodiment.

As shown in FIG. **2**, the memory cell is formed from the switch element T and the magnetoresistive element MTJ arranged on a semiconductor substrate **21**.

The semiconductor substrate **21** is, for example, a silicon substrate, and the conductivity type can be either P or N. In the semiconductor substrate **21**, for example, a silicon oxide layer having an STI structure is arranged as an element isolation insulating layer **22**.

The switch element T is arranged in the surface area of the semiconductor substrate **21**, more specifically, in the element area (active area) surrounded by the element isolation insulating layer **22**. In this example, the switch element T is an FET that includes two source/drain diffusion layers **23** in the semiconductor substrate **21**, and a gate electrode **24** arranged on the channel area between them. The gate electrode **24** functions as the word line WL.

The switch element T is covered with an insulating layer (for example, silicon oxide) **25**. Contact holes are formed in the insulating layer **25**. A contact via (CB) **26** is arranged in each contact hole. The contact via **26** is made of a metal material such as W (tungsten) or Cu (copper).

The lower surface of the contact via **26** is connected to the switch element. In this example, the contact via **26** is in direct contact with the source/drain diffusion layer **23**.

A lower electrode (LE) **27** is arranged on the contact via **26**. The lower electrode **27** has a stacked structure of, for example, Ta (10 nm)/Ru (5 nm)/Ta (5 nm).

The magnetoresistive element MTJ is arranged on the lower electrode **27**, that is, immediately above the contact via **26**. Details of the magnetoresistive element MTJ according to this embodiment will be described later.

An upper electrode (UE) **28** is arranged on the magnetoresistive element MTJ. The upper electrode **28** is made of, for example, TiN. The upper electrode **28** is connected to the bit line (for example, Cu) BLA via a via (for example, Cu) **29**.

2. First Embodiment

A magnetoresistive element MTJ according to the first embodiment will be described with reference to FIGS. **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, and **20**. In the first embodiment, a reference layer interface layer **32** located under a tunnel barrier layer **34** in the magnetoresistive element MTJ includes a magnetized area (first area) **38** at the center portion, and a deactivated area (second area) **39** at the peripheral portion where the magnetization is smaller than that of the magnetized area **38**. The magnetoresistive element MTJ according to the first embodiment will be explained below in detail.

2-1. Structure of First Embodiment

The structure of the magnetoresistive element MTJ according to the first embodiment will be described.

FIGS. **3**A and **3**B shows the structure of the magnetoresistive element MTJ according to the first embodiment. More specifically, FIG. **3**A is a sectional view showing the structure of the magnetoresistive element MTJ, and FIG. **3**B is a plan view showing the structure of the magnetoresistive element MTJ.

As shown in FIG. **3**A, the magnetoresistive element MTJ includes a reference layer **33**, a tunnel barrier layer **34**, a storage layer **35**, a cap layer **36**, and a hard mask (HM) **37**.

The reference layer **33** is formed on an underlying layer (not shown) on the lower electrode **27**. The reference layer **33** is a magnetic layer having an invariable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface. "Invariable magnetization direction" means that the magnetization direction does not change for a predetermined write current.

The reference layer **33** is made of, for example, CoFeB. However, the embodiment is not limited to this. A ferromagnetic material containing at least one element selected from the group consisting of, for example, Co (cobalt), Fe (iron), B (boron) Ni (nickel), Ir (iridium), Pt (platinum), Mn (manganese), and Ru(ruthenium) may be used. Note that the reference layer **33** is made of CoFeB in the amorphous state at the time of formation, and is mainly made of CoFe after crystallization.

The reference layer **33** includes a reference layer main body layer **31** formed on the lower side, and a reference layer interface layer **32** formed on the upper side. That is, the reference layer main body layer **31** is formed on the underlying layer (not shown) on the lower electrode **27**. The reference layer interface layer **32** is formed in contact with the lower portion of the tunnel barrier layer **34**. The reference layer main body layer **31** is the origin of perpendicular magnetic anisotropy. The reference layer interface layer **32** attains lattice matching with respect to the tunnel barrier layer **34** in contact on the upper side. The reference layer main body layer **31** and the reference layer interface layer **32** are made of, for example, the same material (for example, CoFeB) but may have different composition ratios. More specifically, the composition ratio of the reference layer interface layer **32** is adjusted to attain lattice matching with respect to the tunnel barrier layer **34** in contact on the upper side. The reference layer main body layer **31** is not limited to CoFeB and may be made of a ferromagnetic material such as FePd, FePt, CoPd, or CoPt having the L10 structure or L11 structure, a ferrimagnetic material such as TbCoFe, or an artificial lattice formed from a stacked structure of a magnetic material such as Ni, Fe, or Co and a nonmagnetic material such as Cu (copper), Pd (palladium), or Pt. Details of the reference layer interface layer **32** according to the first embodiment will be described later.

"Perpendicular magnetization" means that the direction of residual magnetization is perpendicular or almost perpendicular to the film surface (upper surface/lower surface). In this specification, "almost perpendicular" means that the direction of residual magnetization falls within the range of $45° < \theta \leq 90°$ with respect to the film surface.

The tunnel barrier layer **34** is formed on the reference layer **33**. The tunnel barrier layer **34** is a nonmagnetic layer and is made of, for example, MgO. The tunnel barrier layer **34** comes into contact with the reference layer **33**, thereby generating perpendicular magnetic anisotropy in the interface (reference layer interface layer **32**) to the reference layer **33**. Referring to FIG. **3**, the tunnel barrier layer **34** is formed to a predetermined film thickness. In this embodiment, however, a case in which the tunnel barrier layer **34** is formed nonuniformly at the peripheral portion can be assumed.

The storage layer **35** is formed on the tunnel barrier layer **34**. The storage layer **35** is a magnetic layer having a variable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface. "Variable magnetization direction" means that the magnetization direction changes for a predetermined write current. That is, the magnetization direction reversal threshold of the storage layer **35** is smaller than that of the reference layer **33**.

The size of the storage layer **35** on the plane is smaller than that of the reference layer **33** and the tunnel barrier layer **34**. The planar shape of the magnetoresistive element MTJ is, for example, circular. For this reason, the diameter of the storage layer **35** on the plane is smaller than that of the reference layer **33** and the tunnel barrier layer **34**. The storage layer **35** is located above the central portion of the reference layer **33** and the tunnel barrier layer **34**. Note that the planar shape of the magnetoresistive element MTJ need not always be circular and may be square, rectangular, elliptical, or the like.

The storage layer **35** uses a ferromagnetic material containing at least one element selected from the group consisting of, for example, Co and Fe. In addition, for the purpose of adjusting saturation magnetization, magnetocrystalline anisotropy, or the like, an element such as B (boron), C (carbon), or Si (silicon) may be doped into the ferromagnetic material.

The cap layer **36** is formed on the storage layer **35**. The hard mask **37** is formed on the cap layer **36**. The hard mask is made of a conductive material containing, for example, as a metal. An upper electrode **28** is formed on it.

The magnetoresistive element MTJ is, for example, a spin transfer torque magnetoresistive element. Hence, when writing data to the magnetoresistive element MTJ or reading data from the magnetoresistive element MTJ, a current is bidirectionally supplied to the magnetoresistive element MTJ in the direction perpendicular to the film surface (stacked surface).

More specifically, data write to the magnetoresistive element MTJ is performed in the following way.

When electrons (electrons moving from the reference layer **33** to the storage layer **35**) are supplied from the side of a lower electrode **27**, the electrons are spin-polarized in the same direction as the magnetization direction of the reference layer **33** and injected into the storage layer **35**. In this case, the magnetization direction of the storage layer **35** is aligned to the same direction as the magnetization direction of the reference layer **33**. The magnetization direction of the reference layer **33** and that of the storage layer **35** thus have parallel alignment. In this parallel alignment, the resistance value of the magnetoresistive element MTJ is minimized. This case will be defined as, for example, data "0".

On the other hand, when electrons (electrons moving from the storage layer **35** to the reference layer **33**) are supplied from the side of the upper electrode **28**, the electrons are reflected by the reference layer **33** to be spin-polarized in a direction reverse to the magnetization direction of the reference layer **33** and then injected into the storage layer **35**. In this case, the magnetization direction of the storage layer **35** is aligned to the direction reverse to the magnetization direction of the reference layer **33**. The magnetization direction of the reference layer **33** and that of the storage layer **35** thus have antiparallel alignment. In this antiparallel alignment, the resistance value of the magnetoresistive element MTJ is maximized. This case will be defined as, for example, data "1".

Data read is performed in the following way.

A read current is supplied to the magnetoresistive element MTJ. The read current is set to a value that does not reverse the magnetization direction of the storage layer **35** (a value smaller than the write current). The semiconductor device can perform the memory operation by detecting a change in the resistance value of the magnetoresistive element MTJ at this time.

In the first embodiment, the reference layer interface layer **32** includes a magnetized area **38**, and a deactivated area **39** where the magnetization is smaller than that of the magnetized area **38**. The magnetized area **38** has perpendicular magnetization in the same magnetization direction as in the reference layer main body layer **31**. On the other hand, the deactivated area **39** has magnetization smaller than that of the magnetized area **38**, or preferably has no magnetization.

As shown in FIG. **33**, the magnetized area **38** is provided at the center (inner portion) of the reference layer interface layer **32**, and the deactivated area **39** is provided at the peripheral portion (outer portion) to surround the magnetized area **38**. More specifically, the magnetized area **38** is located under the storage layer **35** and overlaps the storage layer **35** when viewed from the upper side. In other words, the storage layer **35** does not exist above the deactivated area **39**. That is, the diameter of the magnetized area **38** is the same as that of the storage layer **35**. In addition, the inner diameter of the deactivated area **39** is the same as the diameter of the storage layer **35** (the diameter of the magnetized area **38**). The outer diameter of the deactivated area **39** is the same as the diameter of the reference layer main body layer **31** and the tunnel barrier layer **34**. However, the embodiment is not limited to this, and the inner diameter of the deactivated area **39** (the diameter of the magnetized area **38**) may be larger than the diameter of the storage layer **35**.

The deactivated area **39** contains an element (first element) contained in the magnetized area **38**, and another element (second element) different from the element. That is, the deactivated area **39** is formed by using the first element, like the magnetized area **38**, and then doping the second element. The deactivated area **39** contains the second element and thus has magnetization smaller than that of the magnetized area **38** or no magnetization at all. Note that the second element may be doped into the reference layer main body layer **31** as well to form the deactivated area **39** at part of the reference layer main body layer **31** adjacent to the reference layer interface layer **32**.

FIG. **4** is a view showing an example of the principle of magnetization disappearance of the deactivated area **39** according to the first embodiment. FIG. **5** is views showing other examples of the principle of magnetization disappearance of the deactivated area **39** according to the first embodiment.

As shown in FIG. **4**, when the second element (X) is doped into the deactivated area **39**, the second element makes chemical bonds with the first elements (for example, Co and Fe) to form a compound. A nonmagnetic (antiferromagnetic) compound is thus formed, and the magnetization of the deactivated area **39** considerably decreases or disappears.

Alternatively, as shown in FIGS. **5**A and **5**B, when the second element is doped into the deactivated area **39**, the second element enters among the first elements (among the lattice). The crystal structure of the first element changes, and the magnetization of the deactivated area **39** considerably decreases or disappears.

More specifically, the second element enters among the first elements (among Co and Fe) to prolong the Co—Fe interatomic distance, as shown in FIG. **5**A. When the interatomic distance becomes long, the exchange interaction weakens, and the magnetization disappears.

Alternatively, the second element segregates to the grain boundary, and the first elements are separated into magnetic clusters each formed from a plurality of crystal grains, as shown in FIG. **5**B. Superparamagnetism is generated in which the magnetizations of the magnetic clusters cancel each other, and the magnetization disappears.

Note that the compound formation shown in FIG. **4** has chemical stability higher than in the entry among the lattice shown in FIG. **5**, and restoration of magnetization of the compound formation due to element diffusion or lattice rearrangement by an external cause such as heat occurs at low possibility. For this reason, an element that forms a compound with the first element is preferably used as the second element.

N (nitrogen), P (phosphorus), As (arsenic), or Sb (antimony) that is a pnictogen (group V) element, or C (carbon), Si (silicon), or Ge (germanium) that is a group IV element is used as the second element. The embodiment is not limited to those, and He (helium), F (fluorine), B (boron), Zr (zirconium), Tb (terbium), Ti (titanium), Mg (magnesium), S (sulfur), O (oxygen), or the like may also be used. Two or more of these elements may be used.

FIGS. **6**, **7**, **8**, **9**, **10**, and **11** are graphs each showing the relationship between magnetization and the additional element ratio of an element when the element is doped into the deactivated area **39** according to the first embodiment. FIG. **12** is a graph showing the relationship between the doping amount and magnetization when a group IV element and a group V element are doped into the deactivated area **39** according to the first embodiment. FIG. **13** is a graph showing the relationship between the magnetic field and magnetization when a group V element is doped into the deactivated area **39** according to the first embodiment and a comparative example.

As shown in FIGS. **6** and **7**, when a group V element (in this case, P or N) is doped into the deactivated area **39**, the magnetization disappears at an additional element ratio of about 0.3. As shown in FIG. **8**, when a group IV element (in this case, Si) is doped into the deactivated area **39**, the magnetization disappears at an additional element ratio of about 0.5.

On the other hand, as shown in FIGS. **9**, **10**, and **11**, when an element (in this case, B, S, or O) other than the groups IV and V is doped into the deactivated area **39**, the magnetization disappears at an additional element ratio of 0.5 or more.

As described above, when a group V element or a group IV element is doped into the deactivated area **39**, the magnetization can disappear with a smaller amount of element, as compared to the other elements.

As shown in FIG. **12**, when a group V element (in this case, As) is doped into the deactivated area **39**, the magnetization can disappear with a smaller doping amount as compared to a case in which a group IV element (in this case, Ge) is doped. As shown in FIG. **13**, when a group V element (in this case, As) is doped into the deactivated area **39**, the magnetization generated by applying a magnetic field considerably decreases as compared to a case in which no element is doped.

As described above, to make the magnetization of the deactivated area **39** disappear, the deactivated area **39** is most preferably doped with a group V element.

2-2. Structures of Modifications of First Embodiment

The structures of modifications of the magnetoresistive element MTJ according to the first embodiment will be described.

FIG. **14** is a sectional view showing the structure of a first modification of the magnetoresistive element MTJ according to the first embodiment. FIG. **15** is a sectional view showing the structure of a second modification of the magnetoresistive element MTJ according to the first embodiment.

As shown in FIG. **14**, in the first modification of the first embodiment, the tunnel barrier layer **34** is not formed on the deactivated area **39**. In other words, the tunnel barrier layer **34** is formed only on the magnetized area **38** (center) of the reference layer interface layer **32**. That is, the diameter of the tunnel barrier layer **34** is the same as that of the magnetized area **38** and the storage layer **35**. This is because the peripheral portion of the tunnel barrier layer **34** is removed together with the storage layer **35** in an etching process to be described later.

As shown in FIG. **15**, in the second modification of the first embodiment, the tunnel barrier layer **34** is formed to be thinner on the deactivated area **39** than on the magnetized area **38**. In other words, the tunnel barrier layer **34** is formed to be thinner at the peripheral portion than at the center. This is because the peripheral portion of the tunnel barrier layer **34** is partially removed together with the storage layer **35** in an etching process to be described later.

2-3. Manufacturing Method of First Embodiment

A method of manufacturing the magnetoresistive element MTJ according to the first embodiment will be described.

FIGS. **16**, **17**, and **18** are sectional views showing steps in the manufacture of the magnetoresistive element MTJ according to the first embodiment.

First, as shown in FIG. **16**, a reference layer main body layer **31** is formed on an underlying layer (not shown) on a lower electrode **27**. The reference layer main body layer **31** is made of, for example, a ferromagnetic material such as CoFeB, FePd, FePt, CoPd, or CoPt having the L10 structure or L11 structure, a ferrimagnetic material such as TbCoFe, or an artificial lattice formed from a stacked structure of a magnetic material such as Ni, Fe, or Co and a nonmagnetic material such as Cu, Pd, or Pt. The reference layer main body layer **31** is a magnetic layer having an invariable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface.

Next, a reference layer interface layer **32** is formed on the reference layer main body layer **31**. The reference layer interface layer **32** is made of, for example, CoFeB, like the reference layer main body layer **31**, but may have a different composition ratio. The reference layer interface layer **32** is a magnetic layer having an invariable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface, like the reference layer main body layer **31**.

A tunnel barrier layer **34** is formed on the reference layer interface layer **32**. The tunnel barrier layer **34** is made of, for example, MgO and is a nonmagnetic layer.

A storage layer **35** is formed on the tunnel barrier layer **34**. The storage layer **35** is a magnetic layer having a variable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface.

After that, a cap layer **36** is formed on the storage layer **35**. A hard mask **37** is formed on the cap layer **36**. The hard mask **37** is made of a conductive material containing, for example, a metal. However, the embodiment is not limited to this, and the hard mask **37** may be made of an insulating material. After that, a resist pattern is formed on the hard mask **37**. The hard mask **37** is patterned by, for example, IBE (Ion Beam Etching) or RIE (Reactive Ion Etching) using the resist pattern as a mask. The hard mask **37** thus remains at the center, and the upper surface of the cap layer **36** is exposed at the peripheral portion.

As shown in FIG. **17**, the cap layer **36** and the storage layer **35** are patterned by, for example, IBE or RIE using the patterned hard mask **37** as a mask. The cap layer **36** and the storage layer **35** remain at the center, and the upper surface of the tunnel barrier layer **34** is exposed at the peripheral portion.

Note that at this time, the tunnel barrier layer **34** may be patterned or partially patterned at the peripheral portion, as shown in FIG. **14** or **15**. That is, the upper surface of the reference layer interface layer **32** may be exposed at the peripheral portion. Since IBE reduces damage to the etching surface (side surface) of the storage layer **35**, this patterning process is preferably performed by IBE.

As shown in FIG. **18**, an impurity is ion-implanted to the exposed surface (upper surface). More specifically, an impurity is ion-implanted from the upper surface of the tunnel barrier layer **34** exposed at the peripheral portion, and the impurity element is doped into the peripheral portion of the reference layer interface layer **32**. When the tunnel barrier layer **34** is also patterned, the impurity may be ion-implanted directly to the exposed upper surface of the reference layer interface layer **32**. With this process, a magnetized area **38** is formed at the center of the reference layer interface layer **32**, and a deactivated area **39** having small magnetization (or no magnetization) is formed at the peripheral portion.

At this time, the ion implantation is performed perpendicularly to the upper surface of the tunnel barrier layer **34**. However, the embodiment is not limited to this, and the angle may slightly be shifted depending on the manufacturing apparatus. More specifically, any angle that prohibits a large amount of the impurity element from being implanted directly from the side surface of the storage layer **35** is usable.

The impurity element (second element) ion-implanted into the deactivated area **39** is different from the element (first element) contained in the reference layer interface layer **32** (magnetized area **38**). N, P, As, or Sb that is a group V element, or C, Si, or Ge that is a group IV element is used as the second element. The embodiment is not limited to those, and He, F, B, Zr, Tb, Ti, Mg, S, O, or the like may also be used. Two or more of these elements may be used.

A side wall spacer layer (not shown) is formed on the side surfaces of the storage layer **35**, the cap layer **36**, and the hard mask **37**. The tunnel barrier layer **34** and a reference layer **33** are patterned by, for example, IBE or RIE using the side wall spacer layer as a mask. That is, the peripheral portion of the tunnel barrier layer **34** and the peripheral portion of the reference layer **33** (the peripheral portions of the deactivated area **39** and the reference layer main body layer **31**) are etched.

After that, a protective layer (not shown) is formed on the entire surface, and the magnetoresistive element MTJ according to the first embodiment is completed.

2-4. Effect of First Embodiment

According to the first embodiment, in the magnetoresistive element MTJ including the storage layer **35** and the reference layer **33** having a larger diameter, the reference layer interface layer **32** is formed from the magnetized area **38** at the center (inner portion) and the deactivated area **39** at the peripheral portion (outer portion) having magnetization smaller than that of the magnetized area **38**. With this arrangement, even if the peripheral portion (outer portion) of the tunnel barrier layer **34** located between the storage layer **35** and the reference layer interface layer **32** is nonuniformly etched in the patterning process of the storage layer **35**, the magnetization direction of the deactivated area **39** located immediately below is not distorted. It is therefore possible to suppress degradation of the magnetic characteristic of the reference layer **33**. This effect will be described in more detail.

FIG. **19** is a sectional view showing a comparative example of the magnetization direction of the magnetoresistive element MTJ according to the first embodiment. FIG. **20** is a sectional view showing the magnetization direction of the magnetoresistive element MTJ according to the first embodiment.

A case will be examined, in which the peripheral portion, (exposed peripheral portion) of the tunnel barrier layer **34** is nonuniformly etched in the patterning process of the storage layer **35**, and crystal defects occur, as shown in FIGS. **19** and **20**.

According to the comparative example, the deactivated area **39** is not formed at the peripheral portion of the reference layer interface layer **32**, as shown in FIG. **19**. Normally, interface magnetic anisotropy (perpendicular magnetic anisotropy) is generated in the reference layer interface layer **32** that is in contact with the tunnel barrier layer **34**. However, if the peripheral portion of the tunnel barrier layer **34** is nonuniformly etched, the perpendicular magnetic anisotropy at the peripheral portion of the reference layer interface layer **32** located immediately below the tunnel barrier layer **34** disappears. As a result, the magnetization direction at the peripheral portion of the reference layer interface layer **32** becomes unstable, and the magnetization direction of the reference layer main body layer **31** also becomes unstable.

On the other hand, according to the first embodiment, the deactivated area **39** without magnetization is formed at the peripheral portion of the reference layer interface layer **32**, as shown in FIG. **20**. For this reason, even if the peripheral portion of the tunnel barrier layer **34** is nonuniformly etched, the magnetization direction at the peripheral portion (deactivated area **39**) of the reference layer interface layer **32** located immediately below the tunnel barrier layer **34** never becomes unstable. That is, since no magnetization exists in the deactivated area **39** inherently, the magnetization direction of the deactivated area **39** does not become unstable due to the nonuniformity of tunnel barrier layer **34**. As a result, the magnetization direction of the reference layer main body layer **31** does not become unstable, either.

Note that when the deactivated area **39** has small magnetization, and the peripheral portion of the tunnel barrier layer **34** is nonuniformly etched, the magnetization direction of the deactivated area **39** becomes unstable. However, since the magnetization of the deactivated area **39** is small, the influence on the reference layer main body layer **31** is small and substantially negligible.

The perpendicular magnetic anisotropy with respect to the reference layer interface layer **32** disappears not only when the peripheral portion of the tunnel barrier layer **34** is nonuniformly etched but also when the peripheral portion of the tunnel barrier layer **34** is completely removed. That is, the first embodiment is applicable independently of the presence/absence of the peripheral portion of the tunnel barrier layer **34**, and is applicable in various cases in which, for example, the peripheral portion is nonuniformly formed or completely etched.

3. Second Embodiment

A magnetoresistive element MTJ according to the second embodiment will be described with reference to FIGS. **21** and **22**. In the second embodiment, a shift adjustment layer **50** that is a magnetic layer having an invariable magnetization direction reverse to the magnetization direction of a reference layer **33** is formed in the magnetoresistive element MTJ. The magnetoresistive element MTJ according to the second embodiment will be explained below in detail. Note that in the second embodiment, a description of the same points as in the first embodiment will be omitted, and different points will mainly be explained.

3-1. Structure of Second Embodiment

The structure of the magnetoresistive element MTJ according to the second embodiment will be described.

FIG. **21** is a sectional view showing the structure of the magnetoresistive element MTJ according to the second embodiment.

As shown in FIG. **21**, the second embodiment is different from the first embodiment in that the magnetoresistive element MTJ includes the shift adjustment layer **50**.

The shift adjustment layer **50** is formed on an underlying layer (not shown) on a lower electrode **27**. The shift adjustment layer **50** is a magnetic layer having an invariable magnetization direction, and has perpendicular magnetization perpendicular or almost perpendicular to the film surface. The magnetization direction is reverse to that of a reference layer **33**. Hence, the shift adjustment layer **50** can cancel a leakage magnetic field from the reference layer **33** to the storage layer **35**. In other words, the shift adjustment layer **50** has the effect of adjusting the offset of the reversing characteristic for the storage layer **35**, which is caused by the leakage magnetic field from the reference layer **33**, to the reverse direction. The shift adjustment layer **50** is made of, for example, a ferromagnetic material such as FePd, FePt, CoPd, or CoPt having the L10 structure or L11 structure or an artificial lattice formed from a stacked structure of a magnetic material such as Ni, Fe, or Co and a nonmagnetic material such as Cu, Pd, or Pt.

The reference layer **33** is formed on a spacer layer (not shown) on the shift adjustment layer **50**. The diameter of the shift adjustment layer **50** is the same as that of the reference layer **33** (the outer diameter of a deactivated area **39**) and is larger than the diameter of the storage layer **35** (the inner diameter of the deactivated area **39** or the diameter of a magnetized area **38**).

3-2. Structure of Modification of Second Embodiment

The structure of a modification of the magnetoresistive element MTJ according to the second embodiment will be described.

FIG. **22** is a sectional view showing the structure of a modification of the magnetoresistive element MTJ according to the second embodiment.

As shown in FIG. **22**, in the modification of the second embodiment, the shift adjustment layer **50** is formed on the storage layer **35**. A cap layer **36** is formed on the shift adjustment layer **50**. The diameter of the shift adjustment layer **50** is the same as that of the storage layer **35** (the inner diameter of the deactivated area **39** or the diameter of the magnetized area **38**) and is smaller than the diameter of the reference layer **33** (the outer diameter of the deactivated area **39**).

3-3. Manufacturing Method of Second Embodiment

A method of manufacturing the magnetoresistive element MTJ according to the second embodiment will be described.

First, as shown in FIG. **21**, a shift adjustment layer **50** is formed on an underlying layer (not shown) on a lower electrode **27**. The shift adjustment layer **50** is made of, for example, a ferromagnetic material such as FePd, FePt, CoPd, or CoPt having the L10 structure or L11 structure or an artificial lattice formed from a stacked structure of a magnetic material such as Ni, Fe, or Co and a nonmagnetic material such as Cu, Pd, or Pt.

Next, a reference layer main body layer **31**, a reference layer interface layer **32**, a tunnel barrier layer **34**, a storage layer **35**, a cap layer **36**, and a hard mask **37** are sequentially stacked on the shift adjustment layer **50**. The hard mask **37**, the cap layer **36**, and the storage layer **35** are patterned. After that, an impurity element is doped into the peripheral portion of the reference layer interface layer **32**.

A side wall spacer layer (not shown) is formed on the side surfaces of the storage layer **35**, the cap layer **36**, and the hard mask **37**. The tunnel barrier layer **34**, a reference layer **33**, and the shift adjustment layer **50** are patterned by, for example, IBE or RIE using the side wall spacer layer as a mask. That is, the peripheral portion of the tunnel barrier layer **34**, the peripheral portion of the reference layer **33** (the peripheral portions of a deactivated area **39** and the reference layer main body layer **31**), and the peripheral portion of the shift adjustment layer **50** are etched.

After that, a protective layer (not shown) is formed on the entire surface, and the magnetoresistive element MTJ according to the second embodiment is completed.

3-4. Manufacturing Method of Modification of Second Embodiment

A method of manufacturing the modification of the magnetoresistive element MTJ according to the second embodiment will be described.

First, as shown in FIG. **22**, a reference layer main body layer **31**, a reference layer interface layer **32**, a tunnel barrier layer **34**, and a storage layer **35** are sequentially stacked on an underlying layer (not shown) on a lower electrode **27**.

Next, a shift adjustment layer **50** is formed on the storage layer **35**. The shift adjustment layer **50** is made of, for example, a ferromagnetic material such as FePd, FePt, CoPd, or CoPt having the L10 structure or L11 structure or an artificial lattice formed from a stacked structure of a magnetic material such as Ni, Fe, or Co and a nonmagnetic material such as Cu, Pd, or Pt.

A cap layer **36** and a hard mask **37** are sequentially stacked on the shift adjustment layer **50**. The hard mask **37**, the cap layer **36**, the shift adjustment layer **50**, and the storage layer **35** are patterned by, for example, IBE or RIE. After that, an impurity element is doped into the peripheral portion of the reference layer interface layer **32**.

A side wall spacer layer (not shown) is formed on the side surfaces of the storage layer **35**, the shift adjustment layer **50**, the cap layer **36**, and the hard mask **37**. The tunnel barrier layer **34** and a reference layer **33** are patterned by, for example, IBE or RIE using the side wall spacer layer as a mask. That is, the peripheral portion of the tunnel barrier layer **34** and the peripheral portion of the reference layer **33** (the peripheral portions of a deactivated area **39** and the reference layer main body layer **31**) are etched.

After that, a protective layer (not shown) is formed on the entire surface, and the modification of the magnetoresistive element MTJ according to the second embodiment is completed.

3-5. Effect of Second Embodiment

According to the second embodiment, the same effect as in the first embodiment can be obtained.

Additionally, in the second element, the shift adjustment layer **50** having magnetization in a direction reverse to that of the reference layer **33** is formed under the reference layer **33** or on the storage layer **35** in the magnetoresistive element MTJ. This allows to cancel the leakage magnetic field from the reference layer **33** to the storage layer **35** and improve the magnetic characteristic of the magnetoresistive element MTJ.

4. Third Embodiment

A magnetoresistive element MTJ according to the third embodiment will be described with reference to FIG. **23**. In the third embodiment, a reference layer **33** has not a stacked structure of a reference layer interface layer **32** and a reference layer main body layer **31** but an integrated structure thereof. The magnetoresistive element MTJ according to the third embodiment will be explained below in detail. Note that in the third embodiment, a description of the same points as in the first embodiment will be omitted, and different points will mainly be explained.

4-1. Structure of Third Embodiment

The structure of the magnetoresistive element MTJ according to the third embodiment will be described.

FIG. **23** is a sectional view showing the structure of the magnetoresistive element MTJ according to the third embodiment.

As shown in FIG. **23**, the third embodiment is different from the first embodiment in that the reference layer main body layer **31** is not formed.

The reference layer **33** includes only the reference layer interface layer **32** formed on an underlying layer (not shown). The reference layer interface layer **32** is made of, for example, CoFeB. At this time, the reference layer interface layer **32** has perpendicular magnetic anisotropy generated in the interface to a tunnel barrier layer **34** formed on it and also has the function of the reference layer main body layer **31**.

The reference layer **33** (reference layer interface layer **32**) includes a magnetized area **38**, and a deactivated area **39** where the magnetization is smaller than that of the magnetized area **38**. The magnetized area **38** has perpendicular magnetization in an invariable magnetization direction. On the other hand, the deactivated area **39** has magnetization smaller than that of the magnetized area **38**, or preferably has no magnetization.

In the reference layer interface layer **32**, the magnetized area **38** is formed at the center on the upper side (the side of the tunnel barrier layer **34**) and throughout the lower portion. On the other hand, the deactivated area **39** is formed at the peripheral portion on the upper side. That is, the deactivated area **39** surrounds the magnetized area **38** located at the center on the upper side.

Note that the deactivated area **39** may be formed at the peripheral portion on the lower side. That is, the deactivated area **39** may be formed throughout the peripheral portion.

The deactivated area **39** contains an element (first element) contained in the magnetized area **38**, and another element (second element) different from the element. That is, the deactivated area **39** is formed by using the first element, like the magnetized area **38**, and then doping the second element. The deactivated area **39** contains the second element and thus has magnetization smaller than that of the magnetized area **38** or no magnetization at all.

4-2. Manufacturing Method of Third Embodiment

A method of manufacturing the magnetoresistive element MTJ according to the third embodiment will be described.

First, as shown in FIG. **23**, a reference layer interface layer **32** is formed on an underlying layer (not shown) on a lower electrode **27**. The reference layer interface layer **32** is made of, for example, CoFeB. The reference layer interface layer **32** has perpendicular magnetic anisotropy generated in the interface to a tunnel barrier layer **34** formed on it.

The tunnel barrier layer **34**, a storage layer **35**, a cap layer **36**, and a hard mask **37** are sequentially stacked on the reference layer interface layer **32**. The hard mask **37**, the cap layer **36**, and the storage layer **35** are patterned by, for example, IBE or RIE.

Next, an impurity element is doped into the peripheral portion on the upper side of the reference layer interface layer **32** to form a deactivated area **39**.

A side wall spacer layer (not shown) is formed on the side surfaces of the storage layer **35**, the cap layer **36**, and the hard mask **37**. The tunnel barrier layer **34** and a reference layer **33** are patterned by, for example, IBE or RIE using the side wall spacer layer as a mask. That is, the peripheral portion of the tunnel barrier layer **34** and the peripheral portion of the reference layer **33** (the peripheral portions of a deactivated area **39** and the reference layer interface layer **32**) are etched.

After that, a protective layer (not shown) is formed on the entire surface, and the magnetoresistive element MTJ according to the third embodiment is completed.

4-3. Effect of Third Embodiment

According to the third embodiment, the same effect as in the first embodiment can be obtained.

Additionally, in the third element, the reference layer main body layer **31** is not formed as the reference layer **33**. Normally, the reference layer main body layer **31** can be made of not only CoFeB but also an alloy such as CoPt, a ferrimagnetic material such as TbCoFe, or a stacked artificial lattice system such as Co/Pt. That is, the manufacturing process of the reference layer main body layer **31** is more difficult than that of the reference layer interface layer **32**. In the third embodiment, however, the reference layer **33** is formed from only the reference layer interface layer **32**, and the reference layer main body layer **31** whose manufacturing process is difficult need not be formed. For this reason, only the reference layer interface layer **32** made of CoFeB easy to deposit needs to be formed in the manufacturing process. Consequently, the manufacturing process of the reference layer **33** becomes easy.

While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Indeed, the novel embodiments described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions and changes in the form of the embodiments described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the inventions.

What is claimed is:

1. A magnetoresistive element comprising:

a first magnetic layer having a magnetization direction invariable and perpendicular to a film surface;

a tunnel barrier layer formed on the first magnetic layer; and

a second magnetic layer formed on the tunnel barrier layer and having a magnetization direction variable and perpendicular to the film surface,

wherein the first magnetic layer includes an interface layer formed on an upper side in contact with a lower portion of the tunnel barrier layer, and a main body layer formed on a lower side and serving as an origin of perpendicular magnetic anisotropy, and

the interface layer includes a first area provided on an inner side and having magnetization, and a second area provided on an outer side to surround the first area and having magnetization smaller than the magnetization of the first area or no magnetization,

wherein a film thickness of the tunnel barrier layer on the second area is smaller than a film thickness of the tunnel barrier layer on the first area.

2. The element of claim **1**, wherein the second area contains a first element contained in the first area and a second element different from the first element, thereby making the magnetization smaller than the magnetization of the first area.

3. The element of claim **2**, wherein the second element includes one of a group V element and a group IV element.

4. The element of claim **2**, wherein the second element includes at least one of N, P, As, Sb, C, Si, Ge, He, F, B, Zr, Tb, Ti, Mg, S, and O.

5. The element of claim **2**, wherein the second area has the magnetization smaller than the magnetization of the first area as the second element makes a chemical bond with the first element to form a compound, or the second element enters among a lattice formed by the first element to change a crystal structure.

6. The element of claim **1**, wherein a diameter of the first magnetic layer is larger than a diameter of the second magnetic layer, and a diameter of the first area is equal to the diameter of the second magnetic layer.

7. The element of claim **1**, wherein the second magnetic layer does not exist on the second area.

8. The element of claim **1**, further comprising a third magnetic layer that is provided under the first magnetic layer or on the second magnetic layer, has a magnetization direction invariable and reverse to the magnetization direction of the first magnetic layer, and cancels a leakage magnetic field from the first magnetic layer to the second magnetic layer.

9. The element of claim **1**, wherein the tunnel barrier layer does not exist on the second area.

10. A magnetoresistive element comprising:

a first magnetic layer having a magnetization direction invariable and perpendicular to a film surface;

a tunnel barrier layer formed on the first magnetic layer; and

a second magnetic layer formed on the tunnel barrier layer and having a magnetization direction variable and perpendicular to the film surface,

wherein the first magnetic layer includes a first area provided on an inner side on an upper side and having magnetization, and a second area provided on an outer side to surround the first area and having magnetization smaller than the magnetization of the first area or no magnetization,

wherein a film thickness of the tunnel barrier layer on the second area is smaller than a film thickness of the tunnel barrier layer on the first area.

11. The element of claim **10**, wherein the second area contains a first element contained in the first area and a second element different from the first element, thereby making the magnetization smaller than the magnetization of the first area.

12. The element of claim **11**, wherein the second element includes one of a group V element and a group IV element.

13. The element of claim **11**, wherein the second element includes at least one of N, P, As, Sb, C, Si, Ge, He, F, B, Zr, Tb, Ti, Mg, S, and O.

14. The element of claim **11**, wherein the second area has the magnetization smaller than the magnetization of the first area as the second element makes a chemical bond with the first element to form a compound, or the second element enters among a lattice formed by the first element to change a crystal structure.

15. The element of claim **10**, wherein a diameter of the first magnetic layer is larger than a diameter of the second magnetic layer, and a diameter of the first area is equal to the diameter of the second magnetic layer.

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